To Prof. Chas. Doremus
with the compliments of
John Marshall.

A

BRIEF INTRODUCTION

TO

QUALITATIVE ANALYSIS:

FOR USE

IN INSTRUCTION IN CHEMICAL LABORATORIES.

BY

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TRANSLATED FROM THE FOURTH AND FIFTH GERMAN EDITIONS,
WITH ADDITIONS,

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TRANSLATOR'S PREFACE.

THE merit of Medicus' "Qualitative Analysis," and its popularity, which is shown by its having already passed through five editions in the German language, led to this translation.

The translator has taken the liberty of rearranging the elements in the first part of the book into groups, to correspond with their precipitation by group reagents, and also of adding two tables and amplifying the text to the extent of about forty pages.

J. M.

PHILADELPHIA, 1892.

CONTENTS.

INTRODUCTION.

Qualitative analysis treats of the methods of ascertaining the composition of substances and the manner in which their constituents may be separated.

Qualitative analysis determines what bodies are present, but does not refer to their quantity. The latter is the object of quantitative analysis.

The following pages contain a systematic course for the detection of bases and acids, with the requisite preliminary tests, preceded by a brief description of the behavior of the more important bases and acids. The behavior of the rare elements is briefly considered and explained by examples in the Appendix.

I. PROPERTIES OF THE BASES.

FIRST GROUP.

METALS precipitated as chlorides by HCl, hydrochloric acid: **Silver, Mercurous Salts, and Lead.**

SILVER, Ag (ARGENTUM).

Atomic weight, 107.66; valence, I.

White, glittering metal; specific gravity, 10.57; melting-point, 954° C.

$AgNO_3$, argentic nitrate, may be employed in making the tests.

1. HCl, hydrochloric acid, or a soluble chloride precipitates white, curdy AgCl, argentic chloride. At first the liquid becomes milky in appearance, due to the finely-divided particles of precipitate in suspension, but on shaking or heating the liquid the precipitate collects in curdy masses and the liquid becomes clear.

On exposure to sunlight the precipitate turns violet and finally black, due to the liberation of a slight quantity of chlorine. The precipitate is insoluble in HNO_3, nitric acid, but dissolves on agitation in NH_4OH, ammonium hydroxide, with the formation of argent-ammonium chloride:

$$AgCl + NH_4OH = AgNH_3Cl + H_2O,$$

from which solution it may be reprecipitated by the addition of nitric acid:

$$AgNH_3Cl + HNO_3 = AgCl + NH_4NO_3.$$

It is also dissolved by KCN, potassium cyanide, and, in

the absence of free acid, by $Na_2S_2O_3$, sodium hyposulphite (thiosulphite).

2. $NaOH$, sodium hydroxide, as well as KOH, potassium hydroxide, precipitates brownish-gray Ag_2O, argentic oxide, insoluble in excess of either reagent.

3. NH_4OH, ammonium hydroxide, added in small quantity, precipitates brownish-gray Ag_2O, argentic oxide, readily soluble in excess of the reagent, forming $AgNH_3OH$, argentammonium hydroxide:

$$Ag_2O + 2NH_4OH = 2AgNH_3OH + H_2O.$$

4. H_2S, hydrogen sulphide, precipitates black Ag_2S, argentic sulphide, insoluble in dilute acids and in $(NH_4)_2S$, ammonium sulphide. Boiling nitric acid dissolves it, with the formation of $AgNO_3$, argentic nitrate.

5. $(NH_4)_2S$, ammonium sulphide, precipitates black Ag_2S, argentic sulphide, insoluble in dilute acids.

6. K_2CrO_4, potassium chromate, produces a purplish-red precipitate of Ag_2CrO_4, argentic chromate, soluble in ammonium hydroxide and in nitric acid.

7. Na_2HPO_4, sodium hydrogen phosphate, precipitates yellowish, flocculent Ag_3PO_4, argentic phosphate, soluble in ammonium hydroxide and in nitric acid.

8. KI, potassium iodide, precipitates yellowish, curdy AgI, argentic iodide, insoluble in dilute nitric acid, and almost insoluble in ammonium hydroxide.

9. KCN, potassium cyanide, precipitates white, curdy $AgCN$, argentic cyanide, soluble in excess of the reagent and in ammonium hydroxide, insoluble in dilute nitric acid.

10. Compounds of silver fused with Na_2CO_3, sodium carbonate, in the reducing blowpipe flame on charcoal yield a white, ductile globule of metallic silver, usually without an incrustation. Occasionally a slight reddish-brown incrustation of oxide is produced.

MERCURY, Hg (HYDRARGYRUM).

Atomic weight, 199.8; valence, II.

Silver-white metal; specific gravity, 13.59; solidifies at —39.4° C. and boils at 357.2° C.

Mercury forms two series of compounds, named respectively mercurous and mercuric compounds. Hg_2O, mercurous oxide, may be taken as the type of the mercurous, and HgO, mercuric oxide, as the type of the mercuric compounds.

BEHAVIOR OF MERCURY IN THE MERCUROUS CONDITION.

$Hg_2(NO_3)_2$, mercurous nitrate, may be employed in making the tests.

1. HCl, hydrochloric acid, or a soluble chloride precipitates from solutions of mercurous salts white, pulverulent Hg_2Cl_2, mercurous chloride (calomel), insoluble in water and in cold dilute acids, easily soluble in nitro-hydrochloric acid (aqua regia), with the formation of $HgCl_2$, mercuric chloride (corrosive sublimate):

$$3Hg_2Cl_2 + 2HNO_3 + 6HCl = 6HgCl_2 + 2NO + 4H_2O.$$

Ammonium hydroxide converts the Hg_2Cl_2, mercurous chloride, into black NH_2Hg_2Cl, dimercurous ammonium chloride, insoluble in excess of the reagent:

$$Hg_2Cl_2 + 2NH_4OH = NH_2Hg_2Cl + NH_4Cl + 2H_2O.$$

2. NaOH, sodium hydroxide, or KOH, potassium hydroxide, precipitates black Hg_2O, mercurous oxide, insoluble in excess of the reagent.

3. NH_4OH, ammonium hydroxide, produces in solutions of mercurous salts a black precipitate containing nitrogen, depending in composition upon the mercurous salt employed and the conditions under which precipitation has occurred. For example, on adding ammonium hydroxide to a solution of $Hg_2(NO_3)_2$, mercurous nitrate, black $NH_2Hg_2NO_3$, dimer-

curous ammonium nitrate (mercurius solubilis Hahnemanni), is formed:

$Hg_2(NO_3)_2 + 2NH_4OH = NH_2Hg_2NO_3 + NH_4NO_3 + 2H_2O.$
The precipitate is insoluble in excess of the reagent.

4. H_2S, hydrogen sulphide, as well as $(NH_4)_2S$, ammonium sulphide, produces a black precipitate, consisting of a mixture of HgS, mercuric sulphide, and metallic mercury (not Hg_2S, mercurous sulphide). On boiling this precipitate with concentrated nitric acid, a white compound composed of HgS, mercuric sulphide, and $Hg(NO_3)_2$, mercuric nitrate $[Hg_3S_2(NO_3)_2]$,[1] insoluble in nitric acid, is formed, while the liquid (filtrate) contains $Hg(NO_3)_2$, mercuric nitrate. Yellow ammonium sulphide, $(NH_4)_2S_x$, converts the mixture of HgS and metallic mercury wholly into HgS, mercuric sulphide. Yellow sodium sulphide, Na_2S_x, as well as yellow potassium sulphide, K_2S_x, converts the mixture into HgS, mercuric sulphide. The precipitate is soluble in nitro-hydrochloric acid.

5. $SnCl_2$, stannous chloride,[2] added in very small quantity to a concentrated solution of a mercurous salt, precipitates, precisely as any other soluble chloride, white Hg_2Cl_2, mercurous chloride; when added in excess, a grayish precipitate of finely-divided metallic mercury is formed:

$$SnCl_2 + 2HCl + Hg_2(NO_3)_2 = Hg_2 + SnCl_4 + 2HNO_3.$$

6. KI, potassium iodide, added in small quantity to a solution of a mercurous salt, precipitates greenish, flocculent Hg_2I_2, mercurous iodide, which in excess of the reagent dissolves, with the separation of metallic mercury and the formation of soluble $HgI_2(KI)_2$, potassium mercuric iodide; therefore, when much potassium iodide is added to a dilute

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[1] $Hg\!<\!\begin{matrix}S\text{—}HgNO_3\\ S\text{—}HgNO_3.\end{matrix}$

[2] $SnCl_2$, stannous chloride, used as a reagent, always contains some free HCl, hydrochloric acid.

solution of a mercurous salt, there immediately appears a grayish precipitate of metallic mercury.

7. A drop or two of a solution of a mercurous salt placed on clean copper foil produces a discoloration, due to the deposition of metallic mercury, which upon being gently rubbed with the finger becomes silvery white and mirror-like in appearance. On heating the foil over the flame the deposit disappears.

8. Mercurous salts (with the exception of Hg_2Cl_2, mercurous chloride, which volatilizes unchanged), when heated in a small dry glass reduction-tube with dry Na_2CO_3, sodium carbonate, yield a sublimate consisting of globules of metallic mercury.

LEAD, Pb (PLUMBUM).

Atomic weight, 206.39; valence, II.

Bluish-white metal; specific gravity, 11.3; melting-point, 334° C.

$Pb(C_2H_3O_2)_2$, plumbic acetate, may be employed in making the tests.

1. HCl, hydrochloric acid, or a soluble chloride precipitates, in solutions not too dilute, white, flocculent (sometimes crystalline) $PbCl_2$, plumbic chloride; soluble at 12.5° C. in 135 parts of water, and at the boiling-point in 30 parts of water. On cooling the hot saturated aqueous solution, the lead salt crystallizes in glistening rhombic needles. It is insoluble in ammonium hydroxide; soluble with difficulty in dilute acids; easily soluble in strong hydrochloric acid, particularly on heating.

2. NaOH, sodium hydroxide, as well as KOH, potassium hydroxide, precipitates white, flocculent $Pb(OH)_2$, plumbic hydroxide (mixed with a slight quantity of basic lead salt),

—insoluble in ammonium hydroxide; slightly soluble in water; and easily soluble in excess of sodium or potassium hydroxide, with the formation of $Pb(ONa)_2$, sodium plumbite,[1] or $Pb(OK)_2$, potassium plumbite:

$$Pb(OH)_2 + 2NaOH = Pb(ONa)_2 + 2H_2O.$$

3. NH_4OH, ammonium hydroxide, precipitates white, flocculent $Pb(OH)_2$, plumbic hydroxide, insoluble in excess of the reagent.

4. H_2S, hydrogen sulphide, or $(NH_4)_2S$, ammonium sulphide, precipitates black PbS, plumbic sulphide, insoluble in dilute acids. Boiling nitric acid converts it into $Pb(NO_3)_2$, plumbic nitrate; boiling fuming nitric acid oxidizes it to $PbSO_4$, plumbic sulphate, which is almost insoluble in nitric acid. On rapidly passing H_2S, hydrogen sulphide, into a dilute solution of lead containing free hydrochloric acid, cinnabar-red Pb_2SCl_2, plumbic sulphochloride,[2] is often produced. By the further addition of H_2S, the plumbic sulphochloride is converted into black PbS:

$$2PbCl_2 + H_2S = Pb_2SCl_2 + 2HCl;$$
$$Pb_2SCl_2 + H_2S = 2PbS + 2HCl.$$

5. K_2CrO_4, potassium chromate, as well as $K_2Cr_2O_7$, potassium bichromate, precipitates yellow $PbCrO_4$, plumbic chromate (chrome-yellow), insoluble in water and in $HC_2H_3O_2$, acetic acid, difficultly soluble in nitric acid, easily soluble in sodium or potassium hydroxide:

$$PbCrO_4 + 4NaOH = Na_2CrO_4 + Pb(ONa)_2 + 2H_2O.$$

6. H_2SO_4, sulphuric acid, precipitates white, pulverulent $PbSO_4$, plumbic sulphate, soluble in 22,800 parts of pure water at ordinary temperature, less soluble in water containing sulphuric acid, more soluble in the presence of hydrochloric

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[1] $Pb\begin{matrix}\diagup O-Na\\ \diagdown O-Na.\end{matrix}$

[2] $S\begin{matrix}\diagup Pb-Cl\\ \diagdown Pb-Cl.\end{matrix}$

or nitric acid. The precipitate is soluble in warm concentrated sulphuric acid, and separates on diluting the solution with water. It is easily soluble in $NH_4C_2H_3O_2$, ammonium acetate, and in the presence of ammonium hydroxide in $(NH_4)_2C_4H_4O_6$, neutral ammonium tartrate, and from these solutions the lead may be precipitated by K_2CrO_4, potassium chromate, as yellow $PbCrO_4$, plumbic chromate.

7. KI, potassium iodide, produces in solutions not too dilute a yellow, pulverulent precipitate of PbI_2, plumbic iodide, soluble in 1235 parts of cold water and in 194 parts of boiling water. The plumbic iodide separates from a hot saturated solution, to which a small quantity of $HC_2H_3O_2$, acetic acid, has been added, in glistening, golden-yellow, six-sided plates.

8. Na_2HPO_4, sodium hydrogen phosphate, precipitates white, flocculent $Pb_3(PO_4)_2$, plumbic phosphate, soluble in nitric acid and in sodium hydroxide, insoluble in acetic acid.

9. Compounds of lead fused with sodium carbonate in the reducing flame on charcoal yield a white, ductile globule of metallic lead together with a yellow incrustation of PbO, plumbic oxide.

SECOND GROUP.

Metals precipitated from acid solutions as sulphides by H_2S, hydrogen sulphide: **Mercuric Salts, Copper, Bismuth, Arsenic, Antimony, Tin, Cadmium, Gold, and Platinum.**

MERCURY, Hg (HYDRARGYRUM).

Atomic weight, 199.8; valence, II.

BEHAVIOR OF MERCURY IN THE MERCURIC CONDITION.

$HgCl_2$, mercuric chloride, or $Hg(NO_3)_2$, mercuric nitrate, may be employed in making the tests.

1. H_2S, hydrogen sulphide, and also $(NH_4)_2S$, ammonium sulphide, produce in solutions of mercuric salts a white precipitate of $Hg_3S_2Cl_2$[1] or $Hg_3S_2(NO_3)_2$,[2] which, on the further addition of the reagent, becomes yellow, then brown, and finally is converted into black HgS, mercuric sulphide:

$$3HgCl_2 + 2H_2S = Hg_3S_2Cl_2 + 4HCl;$$
$$Hg_3S_2Cl_2 + H_2S = 3HgS + 2HCl.$$

HgS is not dissolved by ammonium sulphide; sometimes, however, on being treated with ammonium sulphide, it is converted from black HgS into red HgS (cinnabar).

Na_2S, sodium sulphide, and K_2S, potassium sulphide (particularly in the presence of sodium or potassium hydroxide), dissolve mercuric sulphide, with the formation of HgS_2Na_2[3] or HgS_2K_2.[4]

Mercuric sulphide is insoluble in boiling hydrochloric acid or in nitric acid, but by the continued action of hot concentrated nitric acid it is converted into the white insoluble double salt $Hg_3S_2(NO_3)_2$ (as in the case of Hg_2S, mercurous sulphide).

Nitro-hydrochloric acid dissolves mercuric sulphide, with the formation of $HgCl_2$, mercuric chloride:

$$3HgS + 6HCl + 2HNO_3 = 3HgCl_2 + 2NO + 4H_2O + S_3.$$

2. NaOH, sodium hydroxide, and KOH, potassium hydroxide, produce a brownish-red precipitate of a basic salt, which, upon further addition of the reagent, is converted into yellow HgO, mercuric oxide.

3. NH_4OH, ammonium hydroxide, produces a white precipitate; thus, in a solution of $HgCl_2$, mercuric chloride, white NH_2HgCl, mercuric ammonium chloride is produced:

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[1] $Hg{<}^{S-HgCl}_{S-HgCl.}$ [2] $Hg{<}^{S-HgNO_3}_{S-HgNO_3.}$

[3] $Hg{<}^{SNa}_{SNa.}$ [4] $Hg{<}^{SK}_{SK.}$

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

4. $SnCl_2$, stannous chloride, added in small quantities to mercuric chloride or to mercuric salts containing a very slight quantity of free hydrochloric acid, precipitates white Hg_2Cl_2, mercurous chloride, which, on the addition of more stannous chloride, is reduced to gray, finely-divided, metallic mercury (very delicate reaction).

5. KI, potassium iodide, precipitates red HgI_2, mercuric iodide, soluble in excess of the reagent, with the formation of $HgI_2(KI)_2$, potassium mercuric iodide.

6. A drop or two of a solution of a mercuric salt placed on clean copper foil produces a discoloration, due to the deposition of metallic mercury, as in the case of mercurous salts. On gently rubbing the spot it becomes mirror-like in appearance, and on heating the foil the spot disappears, due to the volatilization of the mercury.

7. Many of the mercuric salts, when heated in a glass reduction-tube, sublime undecomposed, as, for example, $HgCl_2$, mercuric chloride (corrosive sublimate), while others yield sublimates which, because of an admixture of basic salts, are colored yellow. If the white (or yellow) sublimate be covered with dry sodium carbonate and again heated, red mercuric oxide is produced, which, on being more strongly heated, breaks up into metallic mercury and oxygen.

COPPER, Cu (CUPRUM).

Atomic weight, 63.18; valence, II.

Reddish metal; specific gravity, 8.94; melting-point, 1054° C.

$CuSO_4$, cupric sulphate, may be employed in making the tests.

1. H_2S, hydrogen sulphide, or $(NH_4)_2S$, ammonium sulphide, precipitates black CuS, cupric sulphide, insoluble in dilute

acids, insoluble in Na_2S, sodium sulphide, and in K_2S, potassium sulphide. Ammonium sulphide (particularly the yellow ammonium sulphide) dissolves traces of the precipitate, with the formation of $Cu_2S_7(NH_4)_2 = (CuS)_2(NH_4)_2S_5$. Boiling nitric acid dissolves CuS, with the formation of $Cu(NO_3)_2$, cupric nitrate. It is also soluble in KCN, potassium cyanide:

$$2CuS + 4KCN = Cu_2C_4N_4K_2 + K_2S_2.$$

The precipitate (CuS), when moist and exposed to the air, readily absorbs oxygen, with the formation of $CuSO_4$, cupric sulphate.

2. NaOH, sodium hydroxide, or KOH, potassium hydroxide, produces in cold solution a voluminous flocculent precipitate of bluish-white $Cu(OH)_2$, cupric hydroxide, insoluble in excess of the reagent, but easily soluble in ammonium hydroxide. The precipitate, on being boiled with excess of sodium or potassium hydroxide, loses water and forms black CuO, cupric oxide. On adding sodium or potassium hydroxide to copper solutions containing non-volatile organic acids, and particularly containing such organic substances as glucose, (grape sugar,) glycerin, etc., and agitating the liquid, the bluish-white cupric hydroxide at first produced is immediately dissolved, with the production of a deep-blue liquid.[1]

3. NH_4OH, ammonium hydroxide, added in small quantities, produces a bluish-white precipitate of a basic salt, which is soluble in an excess of the reagent, producing a deep-blue

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[1] This property is made use of in the preparation of an alkaline copper solution in which cupric sulphate solution is added to a strong sodium hydroxide solution containing $KNaC_4H_4O_6$, potassium sodium tartrate (Rochelle salt), the whole forming a deep-blue liquid (Fehling's solution), which is employed as a reagent for the detection of glucose (grape sugar). On boiling a solution containing glucose to which Fehling's solution has been added, insoluble red Cu_2O, cuprous oxide, or yellow $Cu_2(OH)_2$, cuprous hydroxide, separates.

solution, due to the formation of $Cu(NH_3)_4SO_4$, cupric ammonium sulphate (very delicate reaction). Strong acid solutions are not generally precipitated by ammonium hydroxide.

4. Na_2HPO_4, sodium hydrogen phosphate, produces a bluish-green, flocculent precipitate of $Cu_3(PO_4)_2$, soluble in ammonium hydroxide.

5. $K_4Fe(CN)_6$, potassium ferrocyanide, precipitates brownish-red $Cu_2Fe(CN)_6$, cupric ferrocyanide (very delicate reaction).

6. KCN, potassium cyanide, added in excess to a neutral or ammoniacal solution of a salt of copper, produces a colorless solution of $Cu_2(CN)_2(KCN)_2$, potassium cuprous cyanide:

$$Cu(NO_3)_2 + 2KCN = Cu(CN)_2 + 2KNO_3\,;$$

$$2Cu(CN)_2 + 2KCN = \begin{array}{l} Cu{-}C_2N_2{-}K \\ | \\ Cu{-}C_2N_2{-}K \end{array} + C_2N_2.$$

The copper of this potassium salt of hydrocuprocyanic acid[1] is not precipitated by hydrogen sulphide (corresponding to the iron in potassium ferro- and ferricyanide, which is not precipitated by the ordinary reagents).

7. A bright piece of iron (knife-blade) free from grease placed in a solution of copper is soon covered with a reddish deposit of metallic copper.

8. Compounds of copper mixed with sodium carbonate and strongly heated on charcoal in the reducing flame yield reddish spangles or globules of metallic copper.

9. Compounds of copper fused in a bead of borax, $Na_2B_4O_7$, held in a loop of platinum wire in the oxidizing flame of the blowpipe, yield a bluish-green bead. Fused in a bead of sodium ammonium phosphate, $NaNH_4HPO_4$ (microcosmic

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[1] $$\begin{array}{l} Cu{-}C_2N_2{-}H \\ | \\ Cu{-}C_2N_2{-}H. \end{array}$$

salt), they yield, in the oxidizing flame, a bluish-green bead, which, when heated in the reducing flame, becomes reddish brown and opaque, due to the presence of separated metallic copper. The addition to the bead of a little metallic tin facilitates the reduction.

BISMUTH, Bi.

Atomic weight, 207.5; valence, III.

Reddish-white metal; specific gravity, 9.82; melting-point, 270° C.

$Bi(NO_3)_3$ or $BiCl_3$ may be employed in making the tests.

1. H_2S, hydrogen sulphide, or $(NH_4)_2S$, ammonium sulphide, precipitates brownish-black Bi_2S_3, bismuth sulphide, insoluble in dilute acids and in ammonium sulphide. It is dissolved by boiling nitric acid, forming $Bi(NO_3)_3$, bismuth nitrate.

2. NaOH, sodium hydroxide, KOH, potassium hydroxide, or NH_4OH, ammonium hydroxide, precipitates white, amorphous BiO–OH, bismuth hydroxide, insoluble in excess of the reagent.

3. K_2CrO_4, potassium chromate, precipitates yellow, crystalline $Bi_2O(CrO_4)_2$, basic bismuth chromate, insoluble in sodium hydroxide, soluble in nitric acid.

4. A clear solution of a bismuth salt, when poured into a large quantity of water (provided the bismuth solution does not contain too much free acid), produces a milky turbidity, due to the separation of a white basic salt of bismuth. $BiCl_3$, bismuth chloride, yields BiOCl, bismuth oxychloride. $Bi(NO_3)_3$, bismuth nitrate, yields first $BiONO_3$, bismuth oxynitrate, and afterwards, especially on heating the liquid, $Bi_2O_2NO_3OH$.[1]

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[1] $Bi_2O_2<{}^{OH}_{NO_3}$.

A few drops of hydrochloric acid or of NH_4Cl, ammonium chloride, added to a bismuth nitrate solution before it is poured into the water, causes the separation of the bismuth as $BiOCl$, bismuth oxychloride. The reaction with $BiCl_3$ is the more delicate. Tartaric acid does not interfere with this reaction.

5. Bismuth salts, mixed with sodium carbonate and heated in the reducing flame on charcoal, yield brittle globules of metallic bismuth and a yellow incrustation of Bi_2O_3, bismuthous oxide.

ARSENIC, As (ARSENICUM).

Atomic weight, 74.9; valence, III, V.

Steel-gray non-metal; specific gravity, 5.72 at 14° C.

Arsenic forms two compounds with oxygen,—As_2O_3, arsenious oxide or anhydride, and As_2O_5, arsenic oxide or anhydride.

BEHAVIOR OF ARSENIC IN THE ARSENIOUS CONDITION,—AS ARSENIOUS ACID.

As_2O_3, arsenious oxide, which, when dissolved in water, forms H_3AsO_3, arsenious acid, may be employed in making the tests.

1. H_2S, hydrogen sulphide, precipitates, from warm solutions acidulated with hydrochloric acid, yellow As_2S_3, arsenious sulphide, which is soluble in ammonium sulphide and in $(NH_4)_2CO_3$, ammonium carbonate, but is insoluble in hydrochloric acid. Dissolved in ordinary colorless ammonium sulphide it forms $(NH_4)_3AsS_3$, ammonium sulpharsenite, and from this solution it may be reprecipitated by acids as As_2S_3, arsenious sulphide:

$$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S.$$

Dissolved in yellow ammonium sulphide it forms $(NH_4)_3AsS_4$, ammonium sulpharseniate. From this solution it is precipitated by acids as As_2S_5, arsenic sulphide:

$$As_2S_3 + 3(NH_4)_2S + S_2 = 2(NH_4)_3AsS_4;$$
$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S.$$

Ammonium carbonate dissolves As_2S_3 with the formation of ammonium sulpharsenite and ammonium arsenite:

$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 3CO_2.$$

Acids reprecipitate it from this solution as As_2S_3:

$$(NH_4)_3AsS_3 + (NH_4)_3AsO_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2O.$$

As_2S_5, arsenic sulphide, dissolved in ammonium carbonate forms ammonium sulpharseniate and ammonium arseniate:

$$4As_2S_5 + 12(NH_4)_2CO_3 = 5(NH_4)_3AsS_4 + 3(NH_4)_3AsO_4 + 12CO_2.$$

From this solution acids reprecipitate it as As_2S_5:

$$5(NH_4)_3AsS_4 + 3(NH_4)_3AsO_4 + 24HCl = 4As_2S_5 + 24NH_4Cl + 12H_2O.$$

2. $AgNO_3$, argentic nitrate, added to an aqueous solution of arsenious acid and ammonium hydroxide added drop by drop produces a yellow, curdy precipitate of Ag_3AsO_3, argentic arsenite, soluble in nitric acid and in ammonium hydroxide.

3. $CuSO_4$, cupric sulphate, added to an aqueous solution of arsenious acid, and ammonium hydroxide subsequently added drop by drop, produces a greenish, flocculent precipitate of $CuHAsO_3$, cupric arsenite (Scheele's green), soluble in excess of ammonium hydroxide and in acids.

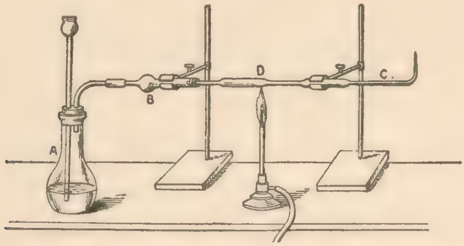
4. *Marsh's Test.*—When a few drops of a solution of arsenious acid or a soluble arsenite are placed in an apparatus in which hydrogen is being evolved, the nascent hydrogen reduces the arsenical compound, and gaseous AsH_3, hydrogen arsenide (arsenuretted hydrogen), is evolved with the free hydrogen:

$$H_3AsO_3 + 3Zn + 3H_2SO_4 = AsH_3 + 3ZnSO_4 + 3H_2O.$$

When this mixture of hydrogen and hydrogen arsenide is

slowly passed through a glass tube heated to incipient redness, the hydrogen arsenide is decomposed, and the arsenic is deposited in the metallic state on the inner surface of the tube just beyond the heated part, as a lustrous brown, gray, or black coating. For this purpose the apparatus of Marsh, Fig. 1, is best adapted.

FIG. 1.



The apparatus consists of a small generating flask, *A*, a drying-tube, *B*,[1] containing small pieces of calcium chloride, and a reduction-tube, *C*, of hard glass, contracted at intervals.

The metallic zinc and concentrated sulphuric acid (diluted with about four volumes of water) used in the operation must be free from arsenic, and therefore the following control test should always be made to determine their purity. Zinc is placed in the flask *A*, and the drying-tube *B*, together with the reduction-tube *C*, is connected with the flask. Dilute sulphuric acid (1–4) is introduced through the funnel-tube until the zinc is covered. When, after some minutes,[2] the evolved hydrogen has expelled the air from the

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[1] The drying-tube is sometimes dispensed with, and the reduction-tube connected directly with the delivery-tube of the flask.

[2] If the action is slow, as is usually the case when pure zinc is employed, it may be accelerated by the addition of a few drops of platinic chloride.

entire apparatus,[1] the flame of a Bunsen burner is applied to that part (at *D*) of the reduction-tube between the contracted portion and the drying-tube, and the tube then heated to incipient redness. After the flame has been applied for several minutes, the contracted part of the reduction-tube is examined for the presence of a brownish, gray, or black lustrous deposit. Should such a deposit be found, it indicates that either the zinc or the sulphuric acid, or both, are contaminated with arsenic and therefore unfit for use in the test.

If no deposit is produced by the above test, the application of the heat is continued, and the solution containing arsenic is introduced into the flask, through the funnel-tube. After the lapse of some minutes the contracted part of the tube immediately beyond the flame is examined for the presence of a brownish, gray, or black deposit.[2] A deposit having formed, the reduction-tube is detached (leaving it open at both ends, to permit the free access of air), inclined over a small flame, and gently heated at the part containing the deposit. The arsenic volatilizes, combines with oxygen, and deposits beyond the part heated, as As_2O_3, arsenious oxide, in minute octahedral crystals.[3]

If the gas is ignited as it escapes from the contracted end of the tube, and the temperature of the flame is reduced by holding a piece of cold porcelain in it, incomplete combustion

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[1] Unless the air is expelled, an explosion, which may cause personal injury, is likely to occur when the flame is applied to the reduction-tube.

[2] Antimony yields a deposit much resembling in color that produced by arsenic. The arsenical deposit is soluble in fresh NaOCl, sodium hypochlorite, whereas the antimony deposit is insoluble in that reagent.

[3] The antimony deposit volatilizes and yields a white sublimate, which is generally amorphous, or consists of minute granules and opaque granular masses; but it may contain well-defined octahedral crystals of Sb_2O_3, antimonious oxide.

occurs, and the arsenic is deposited on the porcelain in the metallic state in lustrous brown, gray, or black spots:

$$2AsH_3 + O_3 = As_2 + 3H_2O.$$

The arsenical deposit is soluble in fresh NaClO, sodium hypochlorite. (Distinction from antimony.)

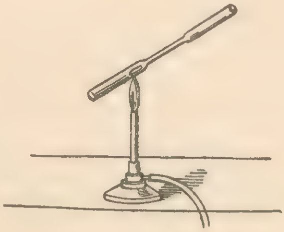
$$As_2 + 3NaOCl + 3H_2O = 2H_3AsO_3 + 3NaCl.$$

As hydrogen arsenide is exceedingly poisonous, it should not be allowed to escape in the room, but should be decomposed by igniting it as it escapes from the tube, or conducting it into a solution of argentic nitrate, whereby reduction of the silver salt occurs with the separation of metallic silver, the arsenic remaining in solution:

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3.$$

5. *Reinsch's Test.*—Metallic copper reduces arsenious oxide in acid solution to metallic arsenic, which is deposited on the copper as Cu_5As_2, cupric arsenide. The arsenical solution is acidulated with about one-seventh of its volume of hydrochloric acid, a clean piece of copper foil placed in the solution, and the whole heated and kept almost at the boiling-point for several minutes. In this hot solution the arsenic is deposited on the foil as a grayish or black coating. The foil is taken from the liquid and immersed several times in water to wash off the hydrochloric acid, then pressed (without rubbing) between filter paper to free it from adherent moisture, and finally completely dried by being heated in a porcelain dish on a water-bath. It is then placed in a reduction-tube near the contracted part, the tube inclined, and the part containing the foil gently heated over a small flame (Fig. 2).

FIG. 2.



Volatilization of the arsenic and combination with oxygen take place, and octahedral crystals of As_2O_3, arsenious oxide, are deposited in the cooler part of the tube.

6. Arsenious oxide heated in a reduction-tube sublimes unchanged, and is deposited in the cooler portion of the tube in octahedral crystals. Heated in a dry reduction-tube with charcoal, a grayish or black mirror-like deposit of metallic arsenic is formed in the cooler part of the tube:

$$As_2O_3 + C_3 = As_2 + 3CO.$$

7. Arsenious oxide or compounds of arsenic heated on charcoal in the reducing flame produce a garlic-like odor. (The arsenious oxide is first reduced to metallic arsenic, which volatilizes and combines with oxygen to form As_2O_3, which sometimes collects as an incrustation on the charcoal.)

8. Arsenious oxide or an arsenite, mixed with six times its bulk of a dry mixture consisting of equal parts of sodium carbonate and potassium cyanide and heated in a reduction-tube, is reduced, with the formation of a black glistening sublimate of metallic arsenic in the cool part of the tube.

BEHAVIOR OF ARSENIC IN THE ARSENIC CONDITION,—AS ARSENIC ACID.

As_2O_5, arsenic oxide, which, dissolved in water, forms H_3AsO_4, arsenic acid; or Na_3AsO_4, sodium arseniate, may be employed in making the tests.

1. H_2S, hydrogen sulphide, does not at first produce a precipitate, but reduces the arsenic acid to arsenious acid. Heating the solution facilitates the reduction:

$$As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + S_2.$$

Continuing the addition of hydrogen sulphide, As_2S_3, arsenious sulphide, is precipitated:

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

The final precipitate is therefore a mixture of arsenious sulphide and sulphur ($As_2S_3 + S_2$).

2. $AgNO_3$, argentic nitrate, added to a solution of arsenic acid which has been exactly neutralized with ammonium hydroxide, or to an arseniate, precipitates reddish-brown Ag_3AsO_4, argentic arseniate, soluble in nitric acid and in ammonium hydroxide:

$$H_3AsO_4 + 3AgNO_3 + 3NH_4OH = Ag_3AsO_4 + 3HN_4NO_3 + 3H_2O.$$

3. $CuSO_4$, cupric sulphate, added to a solution of arsenic acid, followed by the addition of ammonium hydroxide drop by drop, or to an arseniate, produces a bluish-green precipitate of $CuHAsO_4$, cupric arseniate, soluble in an excess of ammonium hydroxide and in acids.

4. The behavior of arsenic acid in Marsh's test or Reinsch's test, in the reduction-tube, mixed with charcoal, and on charcoal itself is identical with arsenious acid.

5. $MgSO_4$, magnesium sulphate, added to a solution of arsenic acid or an arseniate, followed by the addition of NH_4Cl, ammonium chloride,[1] and ammonium hydroxide (magnesia mixture), precipitates white, crystalline $MgNH_4AsO_4 + 6H_2O$, ammonium magnesium arseniate:

$$H_3AsO_4 + MgSO_4 + 3NH_4OH = MgNH_4AsO_4 + (NH_4)_2SO_4 + 3H_2O.$$

In concentrated solutions the precipitate forms immediately, and in dilute solutions gradually; but is always perceptibly crystalline. It is soluble in 15,293 parts of cold water and less soluble in water containing ammonium hydroxide; easily soluble in dilute acids, from which solutions it is reprecipitated by the addition of ammonium hydroxide.

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[1] The addition of ammonium chloride is for the purpose of preventing the precipitation of magnesium hydroxide.

6. NH_4HMoO_4, ammonium molybdate, added to a solution of arsenic acid rather strongly acidulated with nitric acid, and the whole gently warmed, produces a yellow precipitate of, possibly, $(NH_4)_3AsO_4(MoO_3)_{10}$, ammonium molybdoarseniate, soluble in ammonium hydroxide and reprecipitated from this solution by nitric acid. The presence of hydrochloric acid or of chlorides interferes with the delicacy of the reaction.

7. To detect arsenic acid in the presence of arsenious acid (providing the compounds are soluble in water) their behavior with magnesia mixture (compare above, 5) is made use of; arsenious acid produces no precipitate with magnesia mixture. In case the compound is insoluble in water, it is dissolved in hydrochloric acid, and the arsenious acid is precipitated in cold solution with hydrogen sulphide. The resulting arsenious sulphide is removed by filtration, the filtrate is warmed, and hydrogen sulphide again conducted into the liquid. The production of a precipitate indicates the presence of arsenic acid.

ANTIMONY, Sb (STIBIUM).

Atomic weight, 119.6; valence, III, V.

Silvery-white metal; specific gravity 6.7; melting-point, 425° C.

Antimony forms two typical compounds with oxygen,—Sb_2O_3, antimonious oxide, and Sb_2O_5, antimonic oxide.

BEHAVIOR OF ANTIMONY IN THE ANTIMONIOUS CONDITION.

$SbCl_3$, antimonious chloride, may be employed in making the tests.

1. H_2S, hydrogen sulphide, produces in solutions of antimonious salts which are not too strongly acidulated an orange-red precipitate of Sb_2S_3, antimonious sulphide, insoluble in dilute acids, soluble in concentrated hydrochloric acid (without

the separation of sulphur) and also in ammonium sulphide and in sodium or potassium sulphide; insoluble in ammonium carbonate (distinction from arsenic). When dissolved in colorless ammonium sulphide it forms $(NH_4)_3SbS_3$, ammonium sulphantimonite:

$$Sb_2S_3 + 3(NH_4)_2S = 2(NH_4)_3SbS_3;$$

and when dissolved in yellow ammonium sulphide it forms $(NH_4)_3SbS_4$, ammonium sulphantimonate:

$$Sb_2S_3 + 3(NH_4)_2S + S_2 = 2(NH_4)_3SbS_4.$$

Hydrochloric acid precipitates from the sulphantimonite solution Sb_2S_3, and from the sulphantimonate solution Sb_2S_5:

$$2(NH_4)_3SbS_3 + 6HCl = Sb_2S_3 + 6NH_4Cl + 3H_2S;$$
$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S.$$

2. NaOH, sodium hydroxide, as well as KOH, potassium hydroxide, produces a white voluminous precipitate of $Sb(OH)_3$, antimonious hydroxide, readily soluble in an excess of the reagent, forming SbO(ONa), sodium antimonite, or SbO(OK), potassium antimonite. On being boiled in the alkaline liquid the precipitate of $Sb(OH)_3$ is converted into Sb_2O_3, antimonious oxide.

3. NH_4OH, ammonium hydroxide, precipitates white $Sb(OH)_3$, antimonious hydroxide, insoluble in an excess of the reagent. Tartaric acid prevents the precipitation.

4. On pouring a solution of an antimonious salt, as, for example, $SbCl_3$, antimonious chloride, into a large quantity of water, a white precipitate of a mixture of SbOCl, antimonious oxychloride, and $Sb_4O_5Cl_2$ is produced:

$$SbCl_3 + H_2O = SbOCl + 2HCl;$$
$$4SbCl_3 + 5H_2O = Sb_4O_5Cl_2 + 10HCl.$$

A milkiness is produced in water by even the slightest quantity of antimonious chloride. Tartaric acid prevents the precipitation by dissolving the precipitate:

$$SbOCl + H_2C_4H_4O_6 = (SbO)HC_4H_4O_6 + HCl.$$

5. Soluble salts of antimony, placed in a flask in which hydrogen is being generated from zinc and dilute sulphuric acid (1–4), are decomposed, with the formation of gaseous SbH_3, antimonious hydride (antimonuretted hydrogen):

$$2SbCl_3 + Zn_6 + 3H_2SO_4 = 2SbH_3 + 3ZnCl_2 + 3ZnSO_4.$$

The apparatus of Marsh is best adapted for this purpose, and the same precautions as given under arsenic should be observed. (See page 23.)

On heating the reduction-tube of Marsh's apparatus to dull redness and slowly passing antimonious hydride through the tube, the compound is reduced, and a lustrous brown or black deposit of metallic antimony is formed in the part of the tube before the flame, or on both sides of the flame. If the gas is ignited as it escapes from the contracted end of the tube and the temperature of the flame reduced by holding a piece of cold porcelain in it, incomplete combustion occurs, and the antimony is deposited on the porcelain in dull brownish or black spots:

$$2SbH_3 + O_3 = Sb_2 + 3H_2O.$$

The deposit of metallic antimony is insoluble in fresh sodium hypochlorite (distinction from arsenic).

The deposit of metallic antimony in the tube, on being gently heated over a small flame with free access of air,[1] volatilizes, combines with oxygen, and condenses in the cooler part of the tube as white Sb_2O_3, antimonious oxide. The sublimate is usually entirely amorphous, but occasionally may contain octahedral crystals of antimonious oxide.

6. Compounds of antimony in acid solution are reduced on being heated with a piece of bright copper foil, with the deposition of the antimony as a grayish or black coating upon the copper. On washing the foil with water, drying,

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[1] As in Marsh's test for arsenic. (See page 24.)

and gently heating it in a small reduction-tube over a flame, the antimony volatilizes, combines with oxygen, and deposits in the cooler part of the tube as amorphous Sb_2O_3, antimonious oxide, which may sometimes contain octahedral crystals of antimonious oxide. (See Reinsch's Test for Arsenic, page 25.)

7. Metallic zinc reduces antimonious solutions, the antimony separating as a black powder. If a drop of the antimonious solution is placed on a piece of platinum foil and a small fragment of zinc is placed in the solution, the antimony is deposited on the foil as a brown or black adherent coating, insoluble in hydrochloric acid:

$$2SbCl_3 + Zn_3 = Sb_2 + 3ZnCl_2.$$

8. Compounds of antimony, when heated in the reducing flame with sodium carbonate on charcoal, yield a white, brittle globule of metallic antimony, usually coated with a white incrustation of Sb_2O_3, antimonious oxide.

BEHAVIOR OF ANTIMONY IN THE ANTIMONIC CONDITION.

$SbCl_5$, antimonic chloride, may be employed in making the tests.

1. H_2S, hydrogen sulphide, precipitates from acid solutions orange-red Sb_2S_5, antimonic sulphide, insoluble in dilute acids and in ammonium carbonate, soluble in concentrated hydrochloric acid, forming $SbCl_3$, antimonious chloride (with the separation of sulphur):

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + S_2,$$

and soluble in ammonium sulphide and in sodium or potassium sulphide, with the formation of sulphantimonates:

$$Sb_2S_5 + 3(NH_4)_2S = 2(NH_4)_3SbS_4.$$

2. The behavior of antimonic compounds is similar to

that of antimonious compounds in respect to the tests with zinc and dilute sulphuric acid, copper foil and hydrochloric acid, and platinum foil and zinc.

3. To detect antimonious compounds in the presence of antimonic compounds, the behavior of an alkaline solution of antimonious oxide with a silver solution is taken advantage of. On adding argentic nitrate to the alkaline solution and gently heating it, a precipitate composed of Ag_2O, argentic oxide, and metallic silver is formed. Ammonium hydroxide has the property of dissolving only the argentic oxide, leaving the metallic silver undissolved:

$$SbO(OK) + Ag_2O = KSbO_3 + Ag_2.$$

After washing the precipitate and then treating it with ammonium hydroxide, metallic silver will remain undissolved in case an antimonious compound was originally present.

To detect antimonic compounds in the presence of antimonious compounds, the alkaline solution is acidulated with hydrochloric acid, KI, potassium iodide, added, and then boiled; in the presence of an antimonic compound iodine is separated:

$$SbCl_5 + 2HI = SbCl_3 + 2HCl + I_2.$$

TIN, Sn (STANNUM).

Atomic weight, 117.35; valence, II, IV.

Bluish-white metal; specific gravity, 7.29; melting-point, 235° C.

Tin forms two series of compounds, named respectively stannous and stannic compounds. SnO, stannous oxide, may be taken as the type of the stannous, and SnO_2 as the type of the stannic compounds.

BEHAVIOR OF TIN IN THE STANNOUS CONDITION.

$SnCl_2$, stannous chloride, may be employed in making the tests.

1. H_2S, hydrogen sulphide (also ammonium sulphide), precipitates dark-brown SnS, stannous sulphide, insoluble in colorless ammonium sulphide, but easily soluble in yellow ammonium sulphide, with the formation of ammonium sulphostannate, $(NH_4)_2SnS_3$:

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

From this solution acids precipitate yellow SnS_2, stannic sulphide:

$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$

2. NaOH, sodium hydroxide, as well as KOH, potassium hydroxide, precipitates white $Sn(OH)_2$, stannous hydroxide, soluble in excess of the reagent. On boiling a solution of a stannous salt to which an insufficient quantity of sodium or potassium hydroxide has been added, the $Sn(OH)_2$ is converted into black SnO, stannous oxide.

3. NH_4OH, ammonium hydroxide, precipitates white $Sn(OH)_2$, stannous hydroxide, insoluble in excess of the reagent.

4. $HgCl_2$, mercuric chloride, added to an excess of $SnCl_2$, stannous chloride, produces a grayish precipitate of finely-divided metallic mercury:

$$HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

If, on the other hand, an excess of mercuric chloride is added to a stannous chloride solution, a white precipitate of Hg_2Cl_2, mercurous chloride, is formed:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

(a very delicate test and a means of distinction between stannous and stannic salts).

5. A fragment of metallic zinc placed in a solution of stannous chloride precipitates grayish metallic tin:

$$SnCl_2 + Zn = ZnCl_2 + Sn.$$

If performed on platinum foil (see 7 under Antimony, page 31) the tin which separates does not adhere to the platinum foil as a black coating (distinction from antimony).

6. Both stannous salts and stannic salts, when fused with sodium carbonate, or with a mixture of sodium carbonate and potassium cyanide, in the reducing flame on charcoal, yield white, ductile globules of metallic tin together with a slight incrustation of SnO_2, stannic oxide. Stannic oxide moistened with $Co(NO_3)_2$, cobaltous nitrate, and heated in the blowpipe-flame becomes bluish green in color.

BEHAVIOR OF TIN IN THE STANNIC CONDITION.

$SnCl_4$, stannic chloride, may be employed in making the tests.

1. H_2S, hydrogen sulphide, precipitates yellow SnS_2, stannic sulphide, insoluble in ammonium carbonate, but soluble in colorless and also in yellow ammonium sulphide, with the formation of $(NH_4)_2SnS_3$, ammonium sulphostannate. From this solution SnS_2 is reprecipitated on the addition of acids. SnS_2 is soluble in concentrated hydrochloric acid.

2. NaOH, sodium hydroxide, KOH, potassium hydroxide, or NH_4OH, ammonium hydroxide, produces in solutions of stannic salts white precipitates. The precipitate produced in hydrochloric acid solutions of ordinary SnO_2, stannic oxide, is $Sn(OH)_4$, stannic hydroxide, and is easily soluble in dilute sodium or potassium hydroxide; that produced in solutions of metastannic acid is metastannic hydroxide, only slightly soluble in excess of the reagent.

3. Na_2SO_4, sodium sulphate, or NH_4NO_3, ammonium ni-

trate, in saturated solution, added in excess to a hydrochloric acid solution of stannic oxide, precipitates the tin, particularly on the application of heat, as white $Sn(OH)_4$, stannic hydroxide, or as $(Sn(OH)_4)_n$, metastannic hydroxide:

$$SnCl_4 + 4Na_2SO_4 + 4H_2O = Sn(OH)_4 + 4NaCl + 4NaHSO_4;$$
$$SnCl_4 + 4NH_4NO_3 + 4H_2O = Sn(OH)_4 + 4NH_4Cl + 4HNO_3.$$

(Distinction from stannous salts.)

4. Metallic zinc reduces stannic salts in solution to metallic tin in the same manner as it reduces stannous salts. (See 5, page 34.)

CADMIUM, Cd.

Atomic weight, 111.7; valence, II.

Bluish-white metal; specific gravity, 8.54; melting-point, 315° C.

$CdSO_4$, cadmium sulphate, may be employed in making the tests.

1. H_2S, hydrogen sulphide, or ammonium sulphide produces a yellow precipitate of CdS, cadmium sulphide, insoluble in dilute acids, in ammonium and sodium sulphides, and in potassium cyanide, soluble in boiling nitric acid, with the formation of $Cd(NO_3)_2$, cadmium nitrate.

2. NaOH, sodium hydroxide, as well as KOH, potassium hydroxide, precipitates white $Cd(OH)_2$, cadmium hydroxide, insoluble in excess of the reagent.

3. NH_4OH, ammonium hydroxide, precipitates white $Cd(OH)_2$, cadmium hydroxide, soluble in excess of the reagent, probably with the formation of a double salt of cadmium and ammonium, $Cd(ONH_4)_2$.

4. KCN, potassium cyanide, added to a neutral or ammoniacal solution of a cadmium salt, precipitates white $Cd(CN)_2$,

cadmium cyanide, which is soluble in an excess of potassium cyanide, forming a colorless solution of $Cd(CN)_2(KCN)_2$:

$$CdSO_4 + 2KCN = Cd(CN)_2 + K_2SO_4;$$
$$Cd(CN)_2 + 2KCN = Cd(CN)_2(KCN)_2.$$

Hydrogen sulphide precipitates from this solution yellow CdS, cadmium sulphide.

5. Cadmium compounds, mixed with sodium carbonate and fused in the reducing flame on charcoal, yield yellow to brown incrustations of CdO, cadmium oxide.

GOLD, Au (AURUM).

Atomic weight, 196.2; valence, III.

Yellow metal; specific gravity, 19.26; melting-point, 1035° C.

$AuCl_3$, auric chloride, may be employed in making the tests.

1. H_2S, hydrogen sulphide, produces in a cold solution of auric chloride a black precipitate of Au_2S_3, auric sulphide, soluble in ammonium sulphide.

From hot auric chloride solutions hydrogen sulphide precipitates brownish metallic gold:

$$8AuCl_3 + 3H_2S + 12H_2O = Au_8 + 24HCl + 3H_2SO_4.$$

2. NaOH, sodium hydroxide, and also potassium hydroxide precipitate reddish-yellow, amorphous $Au(OH)_3$, auric hydroxide, soluble in excess of the reagent.

3. NH_4OH, ammonium hydroxide, produces a reddish-yellow precipitate of $(NH_3)_2Au_2O_3$, ammonium aurate (fulminating gold):

$$2AuCl_3 + 8NH_4OH = (NH_3)_2Au_2O_3 + 6NH_4Cl + 5H_2O.$$

4. $FeSO_4$, ferrous sulphate, precipitates in the presence of a free mineral acid, even in the cold, but especially on heating,

metallic gold, brownish in color because of its finely-divided condition:

$$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

5. $H_2C_2O_4$, oxalic acid, also precipitates metallic gold from auric chloride solutions:

$$2AuCl_3 + 3H_2C_2O_4 = Au_2 + 6HCl + 6CO_2.$$

The precipitation proceeds slowly, but is complete. Warming the solution facilitates the reduction. The presence of considerable free mineral acid interferes with the precipitation.

6. $SnCl_2$, stannous chloride, especially in very dilute solution, added to auric chloride solutions, produces a purplish-red coloration or a purplish-red precipitate (purple of Cassius), consisting probably of a mixture of finely-divided gold and stannic oxide.

7. Compounds of gold fused with sodium carbonate or with borax on charcoal yield yellow, glistening, ductile spangles of metallic gold.

PLATINUM, Pt.

Atomic weight, 194.3; valence, IV.

Tin-white metal; specific gravity, 21.46; melting-point, 1775° C.

$PtCl_4$, platinic chloride, may be employed in making the tests.

1. H_2S, hydrogen sulphide, produces in cold platinic chloride solutions a brownish coloration, but after some time has elapsed a brownish-black precipitate of PtS_2, platinic sulphide, separates. The precipitate appears at once on heating the solution. The precipitate is insoluble in hydrochloric acid and also in nitric acid, but soluble in nitro-hydrochloric acid (aqua regia) and also in ammonium sulphide.

2. KNO_3, potassium nitrate, to which a drop of hydro-

chloric acid has been added, or potassium chloride, added to a concentrated solution of platinic chloride, produces a yellow, crystalline precipitate of $(KCl)_2PtCl_4$, potassium platinic chloride, slightly soluble in water, insoluble in alcohol. The test is best made in a watch-glass, the liquid being stirred with a glass rod. Alcohol facilitates precipitation.

3. NH_4Cl, ammonium chloride, produces a yellow, crystalline precipitate of $(NH_4Cl)_2PtCl_4$, ammonium platinic chloride, slightly soluble in water, insoluble in alcohol. This test is best made in a watch-glass as in 2, above.

4. Compounds of platinum heated in the reducing flame are reduced to spongy metallic platinum.

THIRD GROUP.

Metals precipitated as hydroxides by NH_4OH, ammonium hydroxide: **Iron, Aluminium, and Chromium.**

IRON, Fe (FERRUM).

Atomic weight, 55.88; valence, II, IV.

Silver-white metal; specific gravity, 7.84.

Iron forms two typical series of compounds, named respectively ferrous and ferric compounds. FeO, ferrous oxide, may be taken as the type of the ferrous compounds, and Fe_2O_3 as the type of the ferric compounds.

BEHAVIOR OF IRON IN THE FERROUS CONDITION.

$FeSO_4$, ferrous sulphate, may be employed in making the tests.

1. NH_4OH, NaOH, or KOH precipitates, in solutions of ferrous salts which are free from dissolved air, white

$Fe(OH)_2$, ferrous hydroxide, which, by the absorption of oxygen, quickly changes in color to green, black, and finally to reddish brown. The presence of ammonium chloride or sulphate retards the precipitation; nevertheless, in these alkaline solutions, in consequence of the absorption of oxygen, black ferrous hydroxide and reddish-brown ferric hydroxide gradually separate.

2. $(NH_4)_2S$ precipitates black FeS, ferrous sulphide, insoluble in excess of the reagent, easily soluble in hydrochloric acid and in nitric acid. Very dilute ferrous solutions are colored green by ammonium sulphide. Moist ferrous sulphide is oxidized on exposure to the air and changes to reddish-brown $Fe_2O(SO_4)_2$, basic ferric sulphate.

3. $K_4Fe(CN)_6$, potassium ferrocyanide, produces in ferrous solutions free from ferric salts a white precipitate, which quickly changes to bluish-white $K_2Fe(Fe(CN)_6)$, potassium ferrous ferrocyanide (Everett's salt), insoluble in acids. On exposure to air the bluish-white precipitate gradually absorbs oxygen and changes to blue $Fe_4(Fe(CN)_6)_3$, ferric ferrocyanide (Prussian blue):

$$4K_2Fe(Fe(CN)_6) + O_2 + 4HCl = Fe_4(Fe(CN)_6)_3 + K_4Fe(CN)_6 + 4KCl + 2H_2O.$$

4. $K_3Fe(CN)_6$, potassium ferricyanide, precipitates dark-blue $Fe_3(Fe(CN)_6)_2$, ferrous ferricyanide (Turnbull's blue), insoluble in acids.

5. KCNS, potassium sulphocyanide, does not produce a claret-red coloration in solutions of ferrous salts free from ferric salts. (Distinction from ferric salts.)

6. Ferrous compounds and also ferric compounds when ignited with sodium carbonate on charcoal yield a black magnetic oxide.

7. All compounds of iron when fused in the oxidizing flame in a bead of borax yield while hot a yellow or reddish-

brown bead, which on cooling becomes lighter in color or colorless. Fused in the reducing flame the bead becomes bottle-green in color.

BEHAVIOR OF IRON IN THE FERRIC CONDITION.

Fe_2Cl_6, ferric chloride, may be employed in making the tests.

1. NH_4OH, $NaOH$, or KOH produces in solutions of ferric salts a voluminous, reddish-brown precipitate of $Fe_2(OH)_6$, ferric hydroxide, insoluble in excess of the reagent and in ammonium salts.

2. $(NH_4)_2S$ precipitates black FeS together with free sulphur:

$$Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$

3. $K_4Fe(CN)_6$, potassium ferrocyanide, precipitates, even in exceedingly dilute solutions of ferric salts, blue $Fe_4(Fe(CN)_6)_3$, ferric ferrocyanide (Prussian blue), insoluble in acids, but decomposed by alkalies.

4. $K_3Fe(CN)_6$, potassium ferricyanide, does not produce a precipitate in ferric solutions, but imparts a green or brown coloration to the solution. (See 3, page 80.)

5. KCNS, potassium sulphocyanide, produces an intense claret-red coloration in ferric solutions, due to the formation of soluble $Fe_2(CNS)_6$, ferric sulphocyanide. In exceedingly dilute solutions the color is pale red. $HgCl_2$, mercuric chloride, destroys the coloration, soluble $Hg(CNS)_2$ being formed.

6. $NaC_2H_3O_2$, sodium acetate, added to a ferric salt colors the solution dark red, due to the formation of $Fe_2(C_2H_3O_2)_6$, ferric acetate, which, on boiling the sufficiently diluted solution, separates with part of the acetic acid as a brownish-red, flocculent precipitate of $Fe_2(OH)_4(C_2H_3O_2)_2$, basic ferric acetate:

$$Fe_2(C_2H_3O_2)_6 + 4H_2O = Fe_2(OH)_4(C_2H_3O_2)_2 + 4HC_2H_3O_2.$$

7. H_2S, hydrogen sulphide, reduces ferric salts in solution to ferrous salts, with the separation of sulphur:

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

8. For the behavior of ferric salts on charcoal and in the borax bead see under Ferrous Salts, 7, page 39.

ALUMINIUM, Al.

Atomic weight, 27.04; valence, IV.

Tin-white metal; specific gravity, 2.56 (spec. grav. of the hammered metal 2.67); melting-point, about 700° C.

$Al_2(SO_4)_3$, aluminium sulphate, or $NH_4Al(SO_4)_2$, ammonium aluminium sulphate (ammonia alum), may be employed in making the tests.

1. NH_4OH precipitates white, gelatinous $Al_2(OH)_6$, aluminium hydroxide, slightly soluble in an excess of the reagent. The precipitation is complete only when the excess of ammonia has been driven off by boiling the solution.

2. NaOH or KOH precipitates gelatinous $Al_2(OH)_6$, aluminium hydroxide, soluble in an excess of either reagent, with the formation of $Al_2O_2(ONa)_2$, sodium aluminate, or $Al_2O_2(OK)_2$ potassium aluminate:

$$Al_2(OH)_6 + 2NaOH = Al_2O_2(ONa)_2 + 4H_2O.$$

As aluminium hydroxide is insoluble in ammonium hydroxide (providing the latter is not present in great excess), the aluminium hydroxide may be reprecipitated from its solution as aluminate by the addition of ammonium chloride:

$$Al_2O_2(ONa)_2 + 2NH_4Cl + 2H_2O = Al_2(OH)_6 + 2NH_3 + 2NaCl.$$

Boiling does not decompose the aluminates. The solutions of aluminates have an alkaline reaction.

3. $(NH_4)_2S$ completely precipitates aluminium from its solution as $Al_2(OH)_6$, aluminium hydroxide, with the evolution of hydrogen sulphide.

4. Na_2HPO_4, sodium hydrogen phosphate, precipitates in neutral solutions white gelatinous $Al_2(PO_4)_2$, aluminium phosphate, insoluble in acetic acid and in ammonium hydroxide, soluble in mineral acids and in sodium or potassium hydroxide, with the formation of aluminates:

$$Al_2(PO_4)_2 + 8NaOH = Al_2O_2(ONa)_2 + 2Na_3PO_4 + 4H_2O.$$

Ammonium chloride reprecipitates the aluminium phosphate from its solution in sodium or potassium hydroxide:

$$Al_2O_2(ONa)_2 + 2Na_3PO_4 + 8NH_4Cl = Al_2(PO_4)_2 + 8NaCl + 8NH_3 + 4H_2O.$$

5. $Na_2S_2O_3$, sodium hyposulphite, added to a neutral solution of a salt of aluminium precipitates white, gelatinous $Al_2(OH)_6$, with the separation of free sulphur and liberation of SO_2, sulphurous anhydride. Complete precipitation takes place only when the solution of the aluminium salt is dilute and is boiled, after the addition of the hyposulphite, until the odor of sulphurous anhydride can no longer be detected:

$$Al_2Cl_6 + 3Na_2S_2O_3 + 3H_2O = Al_2(OH)_6 + 6NaCl + 3SO_2 + S_3.$$

6. Compounds of aluminium, mixed with sodium carbonate and ignited on charcoal, yield white, infusible aluminium oxide; on moistening the mass with cobaltous nitrate and again igniting, an infusible blue residue is obtained, due to the combination of CoO, cobaltous oxide, with Al_2O_3, aluminium oxide (Thenard's blue).

CHROMIUM, Cr.

Atomic weight, 52.45; valence, II, IV.

Light-gray, crystalline powder; specific gravity, 6.81.

Cr_2Cl_6, chromic chloride, may be employed in making the tests.

1. NH_4OH precipitates bluish-gray, gelatinous $Cr_2(OH)_6$,

chromic hydroxide; if the precipitation has taken place in a cold solution, a small quantity of chromic oxide will remain dissolved in the ammonium hydroxide; on boiling this pinkish solution all of the chromium is precipitated as chromic hydroxide.

2. NaOH or KOH precipitates from solutions of both the green and the violet salts of chromium greenish, flocculent $Cr_2(OH)_6$, chromic hydroxide, soluble in an excess of the reagent, forming $Cr_2O_2(ONa)_2$, sodium chromite, and imparting a greenish color to the solution:

$$Cr_2(OH)_6 + 2NaOH = Cr_2O_2(ONa)_2 + 4H_2O.$$

From this solution chromic hydroxide is reprecipitated by the addition of ammonium chloride or by long-continued boiling:

$$Cr_2O_2(ONa)_2 + 4H_2O = Cr_2(OH)_6 + 2NaOH.$$

The precipitated chromic hydroxide obtained by boiling its alkaline solution appears to be insoluble in sodium or potassium hydroxide. It is probably a chromic hydroxide somewhat deficient in water of hydration. The solubility of chromic hydroxide in sodium hydroxide is very much retarded by the presence of ferric oxide.

3. $(NH_4)_2S$ precipitates $Cr_2(OH)_6$, chromic hydroxide, with the evolution of hydrogen sulphide:

$$Cr_2Cl_6 + 3(NH_4)_2S + 6H_2O = Cr_2(OH)_6 + 6NH_4Cl + 3H_2S.$$

4. A salt of chromium, fused on platinum foil with a mixture of sodium carbonate and potassium nitrate or potassium chlorate, yields a mass containing a salt of chromic acid,—*i.e.*, a chromate; on exhausting the mass with water a yellow solution of Na_2CrO_4, sodium chromate, or K_2CrO_4, potassium chromate, is obtained, which when treated with plumbic acetate yields a yellow precipitate of $PbCrO_4$, plumbic chromate:

$$Cr_2O_3 + 2Na_2CO_3 + O_3 = 2Na_2CrO_4 + 2CO_2;$$

$$Na_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2NaC_2H_3O_2.$$

5. Compounds of chromium when ignited with sodium carbonate on charcoal yield a green fused mass containing oxides of chromium.

6. Fused in a bead of borax or of microcosmic salt, in either the oxidizing or the reducing flame, chromium compounds yield a yellowish-green bead, which becomes emerald-green on cooling.

FOURTH GROUP.

Metals precipitated as sulphides from neutral solutions by $(NH_4)_2S$, ammonium sulphide: **Manganese, Zinc, Cobalt, and Nickel.**

MANGANESE, Mn.

Atomic weight, 54.8; valence, II, IV.

Grayish-white metal; specific gravity, about 8.

$MnSO_4$, manganous sulphate, may be employed in making the tests.

1. $(NH_4)_2S$ precipitates pale-salmon-colored MnS, manganous sulphide, containing water, easily soluble in acetic acid and in hydrochloric acid. (Occasionally, especially after standing some time, the pale-salmon-colored precipitate containing water is converted into green MnS, manganous sulphide, which is free from water.) Manganous sulphide readily oxidizes on exposure to the air and becomes dark brown, due to the formation of $MnO(OH)_2$, hydrated peroxide of manganese.

2. NaOH or KOH precipitates white $Mn(OH)_2$, manganous hydroxide, insoluble in excess of the reagent. On exposure to the air the precipitate rapidly becomes brown, due to the

formation of $Mn_2(OH)_6$, manganic hydroxide. Manganous hydroxide is soluble in ammonium chloride, owing to the production of a double salt, whereas manganic hydroxide is insoluble in that reagent; on this account ammonium chloride solutions of manganous hydroxide containing free ammonia become brown on exposure to the air, due to the separation of manganic hydroxide:

$$Mn(OH)_2 + 4NH_4Cl = MnCl_2(NH_4Cl)_2 + 2H_2O + 2NH_3;$$
$$2MnCl_2(NH_4Cl)_2 + 4NH_3 + 5H_2O + O = Mn_2(OH)_6 + 8NH_4Cl.$$

3. NH_4OH precipitates in neutral solutions, and also in solutions free from salts of ammonium, white $Mn(OH)_2$, manganous hydroxide; in the presence of salts of ammonium or of free acids, excess of ammonium hydroxide fails to produce a precipitate, because of the formation of a soluble double salt of manganous hydroxide with the ammonium salts. The action of the oxygen of the air converts the soluble manganous salt into $Mn_2(OH)_6$, manganic hydroxide, which separates as a brown precipitate.

4. Compounds of manganese, fused on platinum foil with sodium carbonate and potassium nitrate, yield a bluish-green mass containing manganates of sodium and potassium:

$$3Mn(OH)_2 + Na_2CO_3 + 4KNO_3 = Na_2MnO_4 + 2K_2MnO_4 + 4NO + CO_2 + 3H_2O.$$

The test is an exceedingly delicate one, and only a minute quantity of a salt of manganese need be used.

On exhausting the mass with water, soluble $KMnO_4$, potassium permanganate, and insoluble brown $MnO(OH)_2$, hydrated peroxide of manganese, are formed:

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + MnO(OH)_2 + 4KOH.$$

The potassium permanganate dissolves, imparting a purplish-red color to the water.

5. Compounds of manganese, fused in the oxidizing flame

in a bead of borax or of microcosmic salt, yield an amethyst-colored bead; fused in the reducing flame, the bead becomes colorless.

ZINC, Zn.

Atomic weight, 64.88; valence, II.

Bluish-white metal; specific gravity, 6.9; melting-point, 433° C.

$ZnSO_4$, zinc sulphate, may be employed in making the tests.

1. $(NH_4)_2S$ precipitates white ZnS, zinc sulphide, easily soluble in hydrochloric acid, insoluble in acetic acid.

2. NaOH or KOH precipitates white, gelatinous $Zn(OH)_2$, zinc hydroxide, soluble in excess of the reagent, with the formation of $Zn(ONa)_2$, sodium zincate, or $Zn(OK)_2$, potassium zincate:

$$Zn(OH)_2 + 2NaOH = Zn(ONa)_2 + 2H_2O.$$

These solutions, which have an alkaline reaction, yield a precipitate of ZnS, zinc sulphide, on the addition of hydrogen sulphide.

3. NH_4OH precipitates in neutral solutions white, flocculent $Zn(OH)_2$, zinc hydroxide, soluble in excess of the reagent.

4. $K_4Fe(CN)_6$, potassium ferrocyanide, produces a white, flocculent precipitate of $Zn_2Fe(CN)_6$, zinc ferrocyanide, insoluble in acids and in ammonium hydroxide. The precipitate while in suspension often has a pale-yellowish appearance, due to the color imparted to the liquid by the presence of an excess of potassium ferrocyanide.

5. Compounds of zinc, ignited with sodium carbonate in the reducing flame on charcoal, yield a coating of ZnO, zinc oxide, which is yellow when hot and white when cold. On moistening the deposit with cobaltous nitrate and again igniting, the deposit becomes green in color.

COBALT, Co.

Atomic weight, 58.6; valence, II, IV.

Steel-gray metal; specific gravity, 8.6.

$Co(NO_3)_2$, cobaltous nitrate, or $CoCl_2$, cobaltous chloride, may be employed in making the tests.

1. $(NH_4)_2S$ precipitates black CoS, cobalt sulphide, insoluble in excess of colorless ammonium sulphide and in dilute hydrochloric acid; soluble in nitro-hydrochloric acid, with the formation of $CoCl_2$, cobaltous chloride:

$$3CoS + 6HCl + 2HNO_3 = 3CoCl_2 + S_3 + 2NO + 4H_2O.$$

2. NaOH or KOH precipitates in cold cobaltous solutions a bluish basic salt, and in boiling solutions rose-red $Co(OH)_2$, cobaltous hydroxide. Both precipitates become oxidized on exposure to the air and turn olive-green in color. They are insoluble in excess of the reagent.

3. NH_4OH precipitates in cold cobaltous solutions a bluish basic salt, and in boiling solutions rose-red $Co(OH)_2$, cobaltous hydroxide. Both of these precipitates are soluble in an excess of the reagent, imparting a reddish color to the liquid, which, on exposure to the oxidizing action of the air, soon changes to brown.

4. KCN, potassium cyanide, precipitates brownish-white $Co(CN)_2$, cobaltous cyanide, soluble in excess of the reagent, with the formation of $(KCN)_2Co(CN)_2$, potassium cobaltous cyanide, from which solution cobaltous cyanide is reprecipitated by hydrochloric acid.

5. KNO_2, potassium nitrite, added in excess to a somewhat concentrated solution of a salt of cobalt, to which sufficient acetic acid has previously been added, produces a yellow, crystalline precipitate of $K_6Co_2(NO_2)_{12}$, potassium cobaltic nitrite $= (KNO_2)_6Co_2(NO_2)_6$:

$$2CoCl_2 + 14KNO_2 + 4HC_2H_3O_2 = K_6Co_2(NO_2)_{12} + 4KC_2H_3O_2 + 4KCl + 2NO + 2H_2O.$$

In concentrated cobalt solutions the precipitate appears immediately, while in dilute solutions it requires some time for it to form.

The presence of free acetic acid is necessary to liberate the nitrous acid (required in the oxidation) from the potassium nitrite. Free hydrochloric acid must not be present; in case of its presence in the solution, it must be neutralized by the addition of $NaC_2H_3O_2$, sodium acetate, previous to the addition of the acetic acid. To insure complete precipitation of the cobalt, particularly in the case of dilute solutions, the solution should be allowed to stand in a warm place for about twenty-four hours.

6. Compounds of cobalt, ignited with sodium carbonate in the reducing flame on charcoal, yield dark, metallic, magnetic spangles.

7. Compounds of cobalt, fused in a bead of borax or of microcosmic salt in either the reducing or the oxidizing flame, impart to the bead a beautiful sapphire-blue color.

NICKEL, Ni.

Atomic weight, 58.6; valence, II, IV.

Silver-white metal; specific gravity, 8.9.

$NiSO_4$, nickelous sulphate, or $NiCl_2$, nickelous chloride, may be employed in making the tests.

1. $(NH_4)_2S$ precipitates black NiS, nickelous sulphide, soluble in excess of ammonium sulphide (particularly in the presence of ammonia), imparting a brownish color to the solution. On boiling the ammonium sulphide solution of nickelous sulphide, it undergoes decomposition (particularly

after the addition of acetic acid), with the separation of the dissolved nickelous sulphide. The precipitate is insoluble in dilute hydrochloric acid, but soluble in nitro-hydrochloric acid.

2. NaOH or KOH precipitates amorphous, apple-green $Ni(OH)_2$, nickelous hydroxide, insoluble in an excess of the reagent.

3. NH_4OH, added in small quantity, precipitates, in neutral solutions of nickelous salts free from ammonium salts, apple-green $Ni(OH)_2$, nickelous hydroxide, soluble in excess of ammonium hydroxide, imparting a bluish color to the solution.

4. KCN, potassium cyanide, precipitates light-green $Ni(CN)_2$, nickelous cyanide, soluble in excess of the reagent, with the formation of $(KCN)_2Ni(CN)_2$, potassium nickelous cyanide. Hydrochloric acid reprecipitates from this solution $Ni(CN)_2$, nickelous cyanide. (Distinction from cobalt.)

5. KNO_2, potassium nitrite (under the conditions given for cobalt, 5, page 47), fails to produce a precipitate in solutions of nickelous compounds.

6. Compounds of nickel, ignited with sodium carbonate on charcoal, yield dark, magnetic, metallic spangles.

7. Compounds of nickel, fused in the oxidizing flame in a bead of borax, yield a bead which is purplish red while hot and pale brownish yellow when cold. In the reducing flame the bead becomes gray and opaque, due to the separation of metallic nickel.

Fused in a bead of microcosmic salt in the oxidizing or the reducing flame, salts of nickel yield a reddish-brown bead which becomes yellow or yellowish red on cooling.

FIFTH GROUP.

Metals precipitated as carbonates from neutral solutions by $(NH_4)_2CO_3$, ammonium carbonate: **Barium, Strontium, and Calcium.**

Complete precipitation does not take place in solutions which were originally acid, or when ordinary commercial ammonium carbonate is employed, unless the solution is boiled after the addition of the ammonium carbonate. Commercial ammonium carbonate consists of equal molecules of NH_4HCO_3, acid ammonium carbonate, and NH_4NH_2COO, ammonium carbamate.[1] Dissolving the commercial carbonate in water converts the ammonium carbamate into neutral ammonium carbonate:

$$NH_4HCO_3 + NH_4NH_2COO + H_2O = NH_4HCO_3 + (NH_4)_2CO_3.$$

In precipitating with ammonium carbonate containing acid ammonium carbonate, part of the precipitate will consist of acid salts,—for example, $Ba(HCO_3)_2$,—which are converted into neutral salts on boiling:

$$Ba(HCO_3)_2 = BaCO_3 + CO_2 + H_2O.$$

BARIUM, Ba.

Atomic weight, 136.86; valence, II.

Silver-white metal; specific gravity, about 4.0.

$BaCl_2$, barium chloride, may be employed in making the tests.

1. $(NH_4)_2CO_3$, ammonium carbonate, precipitates white,

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[1] According to other views, commercial ammonium carbonate consists of one molecule of neutral and two molecules of acid ammonium carbonate, thus:

$$(NH_4)_2CO_3 + 2NH_4HCO_3$$

flocculent $BaCO_3$, barium carbonate. The precipitate is easily soluble in dilute hydrochloric acid, in nitric acid, and in acetic acid, insoluble in pure water, slightly soluble in ammonium chloride, and, like all the carbonates of the alkaline earths, soluble in water containing carbonic acid.

2. H_2SO_4, sulphuric acid, and soluble sulphates, including solutions of calcium and strontium sulphates, precipitate white, finely-pulverulent $BaSO_4$, barium sulphate, insoluble in acids. If the precipitation occur in a cold solution, the particles of the precipitate are so minute that they readily pass through a filter; whereas, if the precipitation take place in a hot solution, the precipitate that is formed is crystalline and readily retained by a filter.

3. $(NH_4)_2C_2O_4$, ammonium oxalate, precipitates white, pulverulent BaC_2O_4, barium oxalate, which when freshly precipitated is soluble in acetic acid and in $H_2C_2O_4$, oxalic acid.

4. Na_2HPO_4, sodium hydrogen phosphate, precipitates white, flocculent $BaHPO_4$, di-basic barium phosphate, soluble in hydrochloric, nitric, and acetic acids.

5. K_2CrO_4, potassium chromate, produces in neutral or acetic acid solutions of salts of barium yellow $BaCrO_4$, barium chromate, soluble in hydrochloric acid and in nitric acid.

6. Compounds of barium, held in the flame of a Bunsen burner by means of a platinum wire, impart a yellowish-green color to the flame.

STRONTIUM, Sr.

Atomic weight, 87.3; valence, II.

Yellowish metal; specific gravity, 2.5.

$Sr(NO_3)_2$, strontium nitrate, may be employed in making the tests.

1. $(NH_4)_2CO_3$, ammonium carbonate, precipitates white

$SrCO_3$, strontium carbonate, easily soluble in dilute hydrochloric acid, in nitric acid, and in acetic acid.

2. H_2SO_4, sulphuric acid, and soluble sulphates, including calcium sulphate, precipitate white, usually crystalline $SrSO_4$, strontium sulphate, insoluble in alcohol. In dilute solutions, and also on using calcium sulphate as the precipitating reagent, the precipitation takes place gradually.

3. $(NH_4)_2C_2O_4$, ammonium oxalate, precipitates white, pulverulent SrC_2O_4, strontium oxalate, soluble with difficulty in acetic acid and in oxalic acid.

4. Na_2HPO_4, sodium phosphate, precipitates white $SrHPO_4$, di-basic strontium phosphate, soluble in hydrochloric, nitric, and acetic acids.

5. K_2CrO_4, potassium chromate, does not produce a precipitate with acid sols of salts of strontium.

6. Compounds of strontium impart a crimson color to the flame.

CALCIUM, Ca.

Atomic weight, 39.9; valence, II.

Yellowish metal; specific gravity, 1.57.

$CaCl_2$, calcium chloride, may be employed in making the tests.

1. $(NH_4)_2CO_3$, ammonium carbonate, precipitates white $CaCO_3$, calcium carbonate, easily soluble in dilute hydrochloric acid, in nitric acid, and in acetic acid.

2. H_2SO_4 and soluble sulphates precipitate immediately, in concentrated solutions of salts of calcium, white, crystalline $CaSO_4$, calcium sulphate, insoluble in alcohol, but soluble in boiling hydrochloric acid. Precipitation takes place in dilute solutions either gradually or not at all.

3. $(NH_4)_2C_2O_4$, ammonium oxalate, precipitates white, pul-

verulent CaC_2O_4, calcium oxalate, easily soluble in hydrochloric or in nitric acid, insoluble in acetic and oxalic acids.

4. Na_2HPO_4, sodium hydrogen phosphate, precipitates white $CaHPO_4$, di-basic calcium phosphate, soluble in hydrochloric, nitric, and acetic acids.

5. K_2CrO_4, potassium chromate, does not produce a precipitate in acid solutions of calcium salts.

6. Compounds of calcium impart a yellowish-red color to the flame.

SIXTH GROUP.

Bases not precipitated by any particular group reagent: **Magnesium, Potassium, Sodium, Ammonium, and Lithium.**

MAGNESIUM, Mg.

Atomic weight, 23.94; valence, II.

Silver-white metal; specific gravity, 1.75.

$MgSO_4$, magnesium sulphate, may be employed in making the tests.

1. NH_4OH precipitates, in neutral solutions of salts of magnesium, part of the magnesium as flocculent $Mg(OH)_2$, magnesium hydroxide, leaving the other part in solution as a double salt of magnesium and ammonium:

$$2MgSO_4 + 2NH_4OH = Mg(OH)_2 + MgSO_4(NH_4)_2SO_4.$$

This double salt is not decomposed by a slight excess of ammonium hydroxide. Compounds of magnesium are not precipitated by ammonium hydroxide in the presence of an excess of ammonium chloride, the latter reagent having the property of dissolving magnesium hydroxide:

$$Mg(OH)_2 + 4NH_4Cl = MgCl_2(NH_4Cl)_2 + 2NH_4OH.$$

2. NaOH or KOH precipitates, particularly on boiling, white $Mg(OH)_2$, magnesium hydroxide.

3. Na_2CO_3, sodium carbonate, or K_2CO_3, potassium carbonate, precipitates $Mg_4(CO_3)_3(OH)_2$, basic magnesium carbonate. (The carbonic acid liberated in the reaction retains part of the magnesium in solution as an acid carbonate; this is precipitated by boiling the solution.) The precipitate is soluble in ammonium chloride.

4. $(NH_4)_2CO_3$ produces no precipitate immediately, but after standing some time a crystalline precipitate of $MgCO_3(NH_4)_2CO_3$ appears. In the presence of a sufficient quantity of ammonium chloride the precipitation does not take place.

5. Na_2HPO_4 produces in concentrated solutions a white, flocculent precipitate of $MgHPO_4$, di-basic magnesium phosphate. If ammonium chloride and ammonium hydroxide are added to the solution of the magnesium salt, and afterwards sodium hydrogen phosphate added, a white, crystalline precipitate of $MgNH_4PO_4$, ammonium magnesium phosphate, is produced:

$$MgSO_4 + Na_2HPO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

The ammonium chloride is added to the solution in order to prevent the precipitation of the magnesium salt by the ammonium hydroxide. The precipitate is always crystalline; in dilute solutions it forms gradually, the formation is facilitated, however, by gently rubbing the inner sides of the vessel with a glass rod.

6. Compounds of magnesium ignited on charcoal are somewhat luminous in the flame. On moistening the mass with cobaltous nitrate and again strongly igniting, a pale-pink color, which is more evident on cooling, is imparted to the mass.

POTASSIUM, K (KALIUM).

Atomic weight, 39.03; valence, I.

Silver-white metal; specific gravity, 0.87; melting-point, 62.5° C.

KNO_3, potassium nitrate, or KCl, potassium chloride, may be employed in making the tests.

1. $PtCl_4$, platinic chloride, precipitates from neutral or acid solutions yellow, crystalline $(KCl)_2PtCl_4$, potassium platinic chloride, slightly soluble in water, insoluble in alcohol. The test is best made in a watch-glass, and the liquid should be stirred with a glass rod. In dilute solutions the precipitate forms slowly. The addition of a little alcohol and, if the potassium salt is not a chloride, a drop of hydrochloric acid facilitates the precipitation.

2. $NaHC_4H_4O_6$, acid sodium tartrate, produces, in rather concentrated neutral solutions of salts of potassium, a white, granular, crystalline precipitate of $KHC_4H_4O_6$, acid potassium tartrate. Stirring the liquid with a glass rod or the addition of alcohol promotes the precipitation. If the potassium solution has an alkaline reaction, it must be neutralized with acetic acid previous to the addition of the acid sodium tartrate. $H_2C_4H_4O_6$, tartaric acid, may be used instead of acid sodium tartrate, but in using it $NaC_2H_3O_2$, sodium acetate, must be added to the solution:

$$KNO_3 + H_2C_4H_4O_6 + NaC_2H_3O_2 = KHC_4H_4O_6 + NaNO_3 + HC_2H_3O_2.$$

In dilute solutions of potassium salts precipitation occurs only after standing some time.

3. Compounds of potassium impart to the flame a violet color.

SODIUM, Na (NATRIUM).

Atomic weight, 22.99; valence, I.

Silver-white metal; specific gravity, 0.97; melting-point, 95.6° C.

NaCl, sodium chloride, may be employed in making the tests.

1. $K_2H_2Sb_2O_7$, potassium pyroantimonate, produces, in neutral or slightly alkaline concentrated solutions of salts of sodium, a white, crystalline precipitate of $Na_2H_2Sb_2O_7$, sodium pyroantimonate. In dilute solutions the precipitate forms only after the liquid has been standing some time. Gently rubbing the inner sides of the vessel facilitates the formation of the precipitate. If the sodium solution have an acid reaction, it must be neutralized with potassium carbonate before the addition of the potassium pyroantimonate. Metals other than sodium or potassium must not be present, as they interfere by forming insoluble antimonates.

2. $PtCl_4$, platinic chloride, as well as $H_2C_4H_4O_6$, tartaric acid, fails to produce a precipitate in solutions of salts of sodium.

3. Compounds of sodium impart to the flame an intense yellow color.

AMMONIUM, NH_4.

The radical NH_4 in its behavior with acid radicals corresponds to potassium and sodium. Another analogy between the radical ammonium and the metals is the existence of an ammonium amalgam.

NH_4Cl, ammonium chloride, may be employed in making the tests.

1. The ammonium salts (in combination with volatile

acids) are characterized by their complete volatility when heated to high temperatures; ammonium borate and ammonium phosphate, however, on being strongly heated leave a residue respectively of boric acid and of phosphoric acid.

2. $PtCl_4$, platinic chloride, precipitates in concentrated solutions yellow, crystalline $(NH_4Cl)_2PtCl_4$, ammonium platinic chloride, slightly soluble in water, insoluble in alcohol. The test is best made in a watch-glass, stirring the liquid with a glass rod. The addition of a little alcohol and, if the ammonium salt is not a chloride, a drop of hydrochloric acid hastens the formation of the precipitate.

3. NaOH or KOH added to a solution of a salt of ammonium liberates ammoniacal gas, on boiling the solution, which may be detected by its odor; by its producing white clouds of ammonium acetate when a glass rod wet with acetic acid is held above the liquid; by its action upon turmeric paper moistened with water, which becomes brown when held above the liquid in which the liberation has occurred; and by its action upon filter paper moistened with mercurous nitrate, which becomes black when held in the evolved gas (due to the formation of black $NH_2Hg_2NO_3$).

4. $H_2C_4H_4O_6$, tartaric acid, or $NaHC_4H_4O_6$, acid sodium tartrate, produces in concentrated solutions of ammonium salts white, crystalline $NH_4HC_4H_4O_6$, acid ammonium tartrate.

(For conditions favoring precipitation see Potassium, 2, page 55.)

LITHIUM, Li.

Atomic weight, 7.0; valence, I.

Silver-white metal; specific gravity, 0.59; melting-point, 180° C.

LiCl, lithium chloride, may be employed in making the tests.

1. Na_2CO_3 precipitates, in cold concentrated solutions of salts of lithium, white Li_2CO_3, lithium carbonate.

2. Na_2HPO_4 added to a solution of a salt of lithium produces a white, crystalline precipitate of Li_3PO_4, lithium phosphate.

3. Compounds of lithium impart to the flame a carmine-red color.

II. PROPERTIES OF THE ACIDS.

FIRST GROUP.

ACIDS which are precipitated by $BaCl_2$, barium chloride, from neutral and from acid solutions: **Sulphuric Acid, Hydrofluosilicic Acid.**

SULPHURIC ACID, H_2SO_4.

(Sulphuric acid combines with bases to form salts called sulphates.)

$MgSO_4$, magnesium sulphate, may be employed in making the tests.

1. The neutral sulphates, with the exception of barium, strontium, calcium, and lead sulphates, are easily soluble in water. Basic sulphates of the heavy metals are soluble in hydrochloric acid or in nitric acid. Lead sulphate and the sulphates of the alkaline earths are decomposed and converted into carbonates by sodium or potassium carbonate.

2. $BaCl_2$, barium chloride, precipitates, from solutions containing sulphates or free sulphuric acid, white, pulverulent $BaSO_4$, insoluble in acids.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates white $PbSO_4$, plumbic sulphate, insoluble in dilute acetic acid, somewhat soluble in boiling concentrated acids. Plumbic sulphate is easily soluble in $(NH_4)_2C_4H_4O_6$, ammonium tartrate; from this solution potassium chromate precipitates the lead as yellow $PbCrO_4$, plumbic chromate.

4. Sulphates, fused with sodium carbonate on charcoal,

yield a residue containing Na_2S, sodium sulphide. On placing a portion of the mass on a clean silver coin and adding a few drops of water, a brownish or black stain of Ag_2S is produced:

$$Na_2SO_4 + C_2 = Na_2S + 2CO_2;$$
$$Na_2S + Ag_2 + 2H_2O = Ag_2S + 2NaOH + H_2.$$

HYDROFLUOSILICIC ACID, H_2SiF_6.

(Hydrofluosilicic acid combines with bases to form salts called silicofluorides.)

Na_2SiF_6, sodium silicofluoride, may be employed in making the tests.

1. Most of the silicofluorides are soluble in water; when gently heated with concentrated sulphuric acid, they evolve gaseous SiF_4, silicon fluoride, and HF, hydrofluoric acid:

$$K_2SiF_6 + H_2SO_4 = SiF_4 + 2HF + K_2SO_4.$$

If a piece of platinum foil containing a drop of water be inverted over the vessel in which the decomposition is effected, the water becomes milky in appearance, due to the formation of insoluble H_2SiO_3, silicic acid:

$$3H_2O + 3SiF_4 = H_2SiO_3 + 2H_2SiF_6.$$

2. $BaCl_2$, barium chloride, precipitates, in solutions of hydrofluosilicic acid and of silicofluorides, crystalline $BaSiF_6$, barium silicofluoride, insoluble in dilute acids.

3. KNO_3, potassium nitrate, precipitates, in solutions that are not too dilute, translucent, gelatinous K_2SiF_6, potassium silicofluoride, soluble with difficulty in water, insoluble in alcohol.

4. NH_4OH produces NH_4F, ammonium fluoride, and H_2SiO_3, silicic acid, both of which are precipitated:

$$6NH_4OH + H_2SiF_6 = H_2SiO_3 + 6NH_4F + 3H_2O.$$

SECOND GROUP.

Acids which are precipitated by $BaCl_2$, barium chloride, in neutral solutions, the barium salts of which are soluble in hydrochloric acid: **Sulphurous Acid, Hyposulphurous Acid, Phosphoric Acid, Boric Acid, Hydrofluoric Acid, Carbonic Acid, Silicic Acid, Chromic Acid, Arsenic Acid, Arsenious Acid.**

SULPHUROUS ACID, H_2SO_3.

(Sulphurous acid combines with bases to form salts called sulphites.)

Na_2SO_3, sodium sulphite, may be employed in making the tests.

1. Of the neutral sulphites only those of the alkalies are soluble in water; the others are easily soluble in acids, with the evolution of SO_2, sulphurous anhydride:

$$BaSO_3 + 2HCl = BaCl_2 + SO_2 + H_2O.$$

2. Dilute acids decompose sulphites, with the evolution of SO_2, sulphurous anhydride, which may be recognized by its odor (that of burning sulphur). The presence of sulphurous anhydride may be detected in gaseous mixtures by its behavior with KIO_3, potassium iodate. A piece of filter paper saturated with a solution of potassium iodate and starch paste, brought while wet in contact with gaseous mixtures containing sulphurous anhydride, becomes blue in color, owing to the reduction of HIO_3, iodic acid, to iodine, and the action of the latter on the starch. By means of the sulphurous anhydride, in the presence of water, the iodic acid is reduced to HI, hydriodic acid:

$$3SO_2 + 3H_2O + HIO_3 = HI + 3H_2SO_4.$$

The hydriodic acid, by the action of the remaining iodic acid, is reduced, with the liberation of free iodine:

$$5HI + HIO_3 = I_6 + 3H_2O.$$

(As the free iodine is reconverted by an excess of sulphurous anhydride into hydriodic acid :

$$I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4,$$

an excess of the sulphurous anhydride causes a disappearance of the color.)

3. $BaCl_2$ precipitates white $BaSO_3$, barium sulphite, soluble in acids.

4. $Pb(C_2H_3O_2)_2$ precipitates white $PbSO_3$, plumbic sulphite, soluble in nitric acid.

5. $AgNO_3$, argentic nitrate, precipitates white Ag_2SO_3, argentic sulphite, soluble in nitric acid. On boiling the precipitate with water, it is decomposed into metallic silver and sulphuric acid, the liquid becoming gray in color, due to the separated metallic silver :

$$Ag_2SO_3 + H_2O = Ag_2 + H_2SO_4.$$

6. $ZnSO_4$, zinc sulphate solution, containing a little $Na_2NOFe(CN)_5$, sodium nitroprusside, added to a solution of a sulphite which, if not neutral, has been neutralized with acetic acid, produces a red coloration ; or a flocculent, purplish-red precipitate, if the solution contain a considerable quantity of the sulphite. When operating with dilute solutions of a sulphite, the test may be made more delicate by the addition of a few drops of potassium ferrocyanide solution. (Distinction from hyposulphites.)

7. H_2S conducted into a solution of sulphurous acid decomposes the latter, with the separation of sulphur and the probable formation of $H_2S_5O_6$, pentathionic acid :

$$5SO_2 + 5H_2S = H_2S_5O_6 + S_5 + 4H_2O.$$

8. Sulphites ignited with sodium carbonate on charcoal yield a yellowish residue containing sodium sulphide, as in the case of sulphates. A portion of the residue placed on a clean silver coin and moistened with a few drops of water produces a brown or black stain of argentic sulphide on the coin.

HYPOSULPHUROUS ACID, $H_2S_2O_3$ (THIOSULPHURIC ACID).

(Hyposulphurous or thiosulphuric acid combines with bases to form salts called hyposulphites or thiosulphites.)

$Na_2S_2O_3$, sodium hyposulphite, may be employed in making the tests.

1. Most of the hyposulphites (thiosulphites) are soluble in water.

2. HCl or H_2SO_4 added to a solution of a hyposulphite liberates $H_2S_2O_3$, hyposulphurous acid, which quickly breaks up into sulphur, sulphurous anhydride, and water:

$$Na_2S_2O_3 + 2HCl = H_2S_2O_3 + 2NaCl;$$
$$H_2S_2O_3 = SO_2 + S + H_2O.$$

Thus hyposulphites, on the addition of either of the above acids, are decomposed and yield sulphurous anhydride, which may be recognized by its odor, and free sulphur.

3. $BaCl_2$, barium chloride, produces in concentrated solutions of hyposulphites a white precipitate of BaS_2O_3, barium hyposulphite, soluble in a large quantity of water. It is also soluble in hydrochloric acid, with the evolution of sulphurous anhydride and the separation of sulphur.

4. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates white PbS_2O_3, plumbic hyposulphite, soluble in nitric acid.

5. $AgNO_3$, argentic nitrate, precipitates white $Ag_2S_2O_3$, argentic hyposulphite, soluble in excess of sodium hyposulphite solution:

$$Ag_2S_2O_3 + Na_2S_2O_3 = 2NaAgS_2O_3.$$

The precipitate becomes almost immediately yellow, then brown, and finally black, due to the formation of argentic sulphide:

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

6. Fe_2Cl_6, ferric chloride, immediately colors hyposulphite solutions reddish violet. (Distinction from sulphites.)

7. Hyposulphites ignited with sodium carbonate on charcoal yield a residue containing sodium sulphide, as in the case of sulphates and of sulphites. A portion of the residue placed on a clean silver coin and moistened with water produces a brown or black stain of argentic sulphide.

PHOSPHORIC ACID, H_3PO_4.

(Phosphoric acid combines with bases to form salts called phosphates.)

Na_2HPO_4, sodium hydrogen phosphate, may be employed in making the tests.

1. The phosphates of the alkalies are soluble in water, the others are soluble in acids.

2. $BaCl_2$, barium chloride, precipitates in solutions of the neutral phosphates white $BaHPO_4$ or $Ba_3(PO_4)_2$, soluble in hydrochloric acid or in nitric acid.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates white $Pb_3(PO_4)_2$, soluble in nitric acid.

4. $AgNO_3$, argentic nitrate, produces in solutions of the phosphates a light-yellow precipitate of $Ag_3(PO_4)$, soluble in nitric acid and in ammonium hydroxide.

5. NH_4Cl, ammonium chloride, NH_4OH, ammonium hydroxide, and $MgSO_4$, magnesium sulphate,[1] added in turn to a solution of a phosphate, produce a white, crystalline precipitate of $MgNH_4PO_4$, ammonium magnesium phosphate:

$$Na_2HPO_4 + NH_4OH + MgSO_4 = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

(The ammonium chloride is added to prevent the precipitation of the magnesium as magnesium hydroxide by the ammo-

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[1] The three reagents composing the so-called "magnesia mixture."

nium hydroxide.) The precipitate is sparingly soluble in pure water, and very slightly soluble in water containing ammonium hydroxide. In precipitating very dilute solutions the precipitate forms more rapidly when the inner sides of the vessel are gently rubbed with a glass rod.

6. NH_4HMoO_4, ammonium molybdate, added in excess, with a considerable quantity of nitric acid, to a solution of phosphoric acid or a phosphate, produces a yellow precipitate, probably of $(NH_4)_3PO_4(MoO_3)_{10}$, ammonium phosphomolybdate:

$$10NH_4HMoO_4 + H_3PO_4 + 7HNO_3 = (NH_4)_3PO_4(MoO_3)_{10} + 7NH_4NO_3 + 10H_2O.$$

The precipitate is insoluble in dilute nitric acid, but easily soluble in ammonium hydroxide; it is reprecipitated from the ammoniacal solution by the addition of excess of nitric acid. The precipitate is also soluble in excess of a phosphate, and thus is explained the non-appearance of a precipitate when only a little ammonium molybdate is added to a solution containing much phosphoric acid. In dilute solutions the precipitate forms slowly. The precipitation is hastened by warming the solution to a temperature of 40° C. A higher temperature should be avoided.

(Pyrophosphates yield with argentic nitrate white precipitates of $Ag_4P_2O_7$, argentic pyrophosphate. Metaphosphates likewise yield white precipitates of $AgPO_3$. Only the metaphosphates coagulate albumen.)

BORIC ACID, H_3BO_3.

(Boric acid combines with bases to form salts called borates.)

$Na_2B_4O_7$, sodium biborate (borax), may be employed in making the tests.

1. Of the borates those of the alkalies are easily soluble in water.

2. $BaCl_2$, barium chloride, produces in concentrated solutions of borates white $Ba(BO_2)_2$, barium metaborate, easily soluble in excess of barium chloride and in ammonium chloride:

$$Na_2B_4O_7 + 2BaCl_2 + H_2O = 2Ba(BO_2)_2 + 2NaCl + 2HCl.$$

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates in concentrated solutions white $Pb(BO_2)_2$, lead ~~barium~~ metaborate, soluble in excess of the reagent.

4. $AgNO_3$, argentic nitrate, precipitates in concentrated solutions of neutral borates white $AgBO_2$, argentic metaborate, which is occasionally tinged with yellow, due to the presence of argentic oxide. In solutions of acid borates the precipitate is $Ag_6B_8O_{15}$. Both precipitates are easily soluble in nitric acid.

5. Boric acid, in the powdered condition, placed in a porcelain dish and covered with alcohol gives a greenish flame on igniting the alcohol. Borates, in the powdered condition, impart the same greenish color to the flame, but must be moistened with a few drops of concentrated sulphuric acid before the addition of the alcohol. The greenish color imparted to the flame is due to $(C_2H_5)_3BO_3$, the ethyl ester of boric acid, formed in the reaction. Boric acid (without the addition of alcohol) when strongly heated on platinum wire imparts a greenish color to the flame. (Compounds of barium and of copper and compounds containing chlorine interfere with the test.)

6. Turmeric paper dipped in an aqueous solution of boric acid, or in a solution of a borate acidified with hydrochloric acid, and warmed until dry, becomes reddish brown in color. On bringing dilute sodium or potassium hydroxide solution in contact with the reddish-brown paper, the color becomes blue and then greenish black.

HYDROFLUORIC ACID, HF.

(Hydrofluoric acid combines with bases to form salts called fluorides.)

KF, potassium fluoride, or NaF, sodium fluoride, may be employed in making the tests.

1. Of the fluorides those of the alkalies are easily soluble in water, the others are soluble only with great difficulty.

2. $BaCl_2$ precipitates from solutions of fluorides white BaF_2, soluble in hydrochloric acid; $Pb(C_2H_3O_2)_2$ precipitates white PbF_2, easily soluble in nitric acid; and $AgNO_3$ precipitates white AgF, also easily soluble in water.

3. $CaCl_2$, calcium chloride, precipitates white, gelatinous CaF_2, calcium fluoride, almost insoluble in water, soluble with difficulty in mineral acids.

4. Hydrofluoric acid has the property of etching glass, forming with the silicic oxide of the glass volatile SiF_4, silicon fluoride:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

The test is performed in a platinum crucible covered with a watch-glass. The convex side of the watch-glass is covered with melted wax, and, after the wax has cooled, a design or figure is, by means of a sharpened piece of wood or the point of a knife-blade, graven of sufficient depth in the wax to expose an uncoated surface of glass. The pulverized fluoride is placed in the crucible, moistened with concentrated sulphuric acid, quickly covered with the watch-glass (waxed side down), and the whole placed on a moderately warm iron plate or porcelain dish.[1] After some time the watch-glass is taken from the crucible, and when the wax

[1] The watch-glass should be filled with cold water, to prevent the melting of the wax.

is removed the graven design will appear etched in the glass.

5. In decomposing fluorides containing considerable silicic acid with concentrated sulphuric acid, gaseous SiF_4 is evolved, which, when conducted through a glass tube moistened with water, undergoes decomposition, rendering the water turbid, with the deposition of silicic acid:

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

The result of the reaction is especially observable on drying the tube.

CARBONIC ACID, H_2CO_3.

(Carbonic acid combines with bases to form salts called carbonates.)

Na_2CO_3, sodium carbonate, may be employed in making the tests.

1. The carbonates of the alkalies are soluble in water, the other carbonates are insoluble in water. Many of the latter are, however, soluble in water containing carbon dioxide, forming acid carbonates:

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2.$$

Carbonates in general readily dissolve in dilute acids, with effervescence (due to the liberation of carbon dioxide). The metal of the carbonate forms a salt with the acid used as a solvent:

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O.$$

2. HCl or any dilute acid (except hydrocyanic acid), added to a carbonate either in solution or in the solid condition,[1] produces effervescence, due to the evolution of carbon dioxide.

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[1] The minerals magnesite ($MgCO_3$), dolomite ($CaCO_3, MgCO_3$), and siderite ($FeCO_3$) produce effervescence with a dilute acid only after being warmed.

The latter may be detected by inclining the test-tube in which the effervescence has taken place so as to pour only the gaseous CO_2 into another test-tube containing clear calcium hydroxide solution. The CO_2, being specifically heavier than air, displaces the air in the tube containing calcium hydroxide, and, on closing the latter tube with the thumb and agitating the liquid, a turbidity is produced, due to the formation of $CaCO_3$, calcium carbonate:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O.$$

3. $BaCl_2$, barium chloride, precipitates white $BaCO_3$, barium carbonate; $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates white $PbCO_3$; both are soluble with effervescence in dilute acids.

4. $AgNO_3$, argentic nitrate, precipitates white Ag_2CO_3, argentic carbonate, which in a little time becomes yellowish, and on being boiled with an excess of sodium carbonate changes to brownish-gray Ag_2O, argentic oxide. The argentic oxide is soluble in ammonium hydroxide and in ammonium carbonate.

SILICIC ACID, H_2SiO_3.

(Silicic acid combines with bases to form salts called silicates.)

Na_2SiO_3, sodium silicate, may be employed in making the tests.

1. Of the silicates only those of the alkalies are soluble in water, the others are partially soluble in concentrated acids.

The addition of an acid (as hydrochloric acid) to a solution of a silicate of an alkali causes the separation of silicic acid, which, if the solution is of sufficient concentration, appears as a gelatinous precipitate; ammonium chloride also separates silicic acid from solutions of silicates of the alkalies:

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl;$$
$$Na_2SiO_3 + 2NH_4Cl + 2H_2O = H_2SiO_3 + 2NaCl + 2NH_4OH.$$

The silicic acid separated in this manner is somewhat soluble in dilute acids. On evaporating the solution containing silicic acid—*i.e.*, the solution with the precipitate in suspension—to the dryness of dust on a water-bath, the silicic acid loses water and amorphous silicic acids are produced,—*i.e.*, polysilicic acids, $H_2Si_4O_9$, for example, which are entirely insoluble in water:

$$4H_2SiO_3 = H_2Si_4O_9 + 3H_2O.$$

On extracting the residue with water containing a little hydrochloric acid, the metal which had originally been in combination with the silicic acid is dissolved as a chloride, while the silicic acid remains undissolved. Evaporation over a free flame is not advised, as thereby (because of the stability of silicic acid when heated) a part of the salt might be reconverted into silicates, as, for example:

$$H_2Si_4O_9 + 2NaCl = Na_2Si_4O_9 + 2HCl.$$

For the methods employed in dissolving and disintegrating silicates insoluble in water, see Silicates, page 112.

2. $BaCl_2$, barium chloride, precipitates in solutions of silicates of the alkalies white $BaSiO_3$, barium silicate; $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates white $PbSiO_3$, plumbic silicate; $AgNO_3$, argentic nitrate, precipitates yellowish Ag_2SiO_3, argentic silicate; all soluble in acids, the argentic silicate being also soluble in ammonium hydroxide.

3. NH_4HMoO_4, ammonium molybdate, together with an excess of nitric acid, added to a solution of a silicate produces a yellowish coloration, and, in the presence of considerable ammonium chloride, a lemon-yellow precipitate. Warming facilitates the reaction.

4. On fusing a silicate with microcosmic salt in the loop of a platinum wire, the sodium metaphosphate which is produced

dissolves the base, while the silicic acid remains undissolved and swims in small opaque particles in the otherwise transparent bead while the latter is in a state of fusion ("skeleton of silica"); for example:

$$CaSiO_3 + NaPO_3 = CaNaPO_4 + SiO_2.$$

Uncombined silicic acid produces the same result. The reaction is made more evident by coloring the bead with a compound of copper or of iron.

ARSENIOUS ACID, H_3AsO_3. (See page 21.)

ARSENIC ACID, H_3AsO_4. (See page 26.)

CHROMIC ACID, H_2CrO_4.

(Chromic acid combines with bases to form salts called chromates.)

K_2CrO_4, potassium chromate, may be employed in making the tests.

1. Most of the chromates are insoluble in water. The chromates of the alkalies (the neutral salts) are easily soluble; the bichromates (the so-called acid salts) are soluble, with the production of a reddish-yellow color.

2. $BaCl_2$, barium chloride, precipitates from solutions of chromates yellow $BaCrO_4$, barium chromate, soluble with great difficulty in water, soluble in hydrochloric and in nitric acids.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates yellow, crystalline $PbCrO_4$, plumbic chromate (chrome-yellow), insoluble in water and in acetic acid, soluble in nitric acid and in sodium hydroxide, in the latter with the formation of Na_2CrO_4, sodium chromate, and $Pb(ONa)_2$, sodium plumbite; acetic acid reprecipitates lead chromate from the sodium hydroxide solution.

4. $AgNO_3$, argentic nitrate, precipitates in solutions of chromates purplish-red Ag_2CrO_4, argentic chromate, and in solutions of bichromates purplish-red $Ag_2Cr_2O_7$, argentic bichromate, both soluble in nitric acid and in ammonium hydroxide.

5. H_2S, hydrogen sulphide, conducted into a solution of a chromate containing considerable free hydrochloric acid or sulphuric acid, reduces the chromate, with the formation of a soluble chromic salt and the separation of sulphur, the solution at the same time becoming green in color:

$$2K_2CrO_4 + 3H_2S + 10HCl = Cr_2Cl_6 + S_3 + 4KCl + 8H_2O.$$

In case the acid is present in small quantity, greenish $Cr_2(OH)_6$, chromic hydroxide, or (especially on warming the solution) brown chromium chromate is precipitated:

$$2K_2CrO_4 + 3H_2S + 4HCl = Cr_2(OH)_6 + S_3 + 4KCl + 2H_2O;$$

$$3K_2CrO_4 + 3H_2S + 6HCl = (CrO)_2CrO_4 + S_3 + 6KCl + 6H_2O.$$

The action of ammonium sulphide in neutral or alkaline solutions of chromates is similar to that of hydrogen sulphide.

6. On adding C_2H_5OH, alcohol, to a solution of a chromate or bichromate containing free hydrochloric or sulphuric acid, and warming the liquid, the chromate is reduced to a chromic salt, while the alcohol is oxidized to C_2H_4O, aldehyde; in consequence, the liquid becomes green in color and the odor of aldehyde becomes evident:

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5OH = Cr_2(SO_4)_3 + 3C_2H_4O + K_2SO_4 + 7H_2O.$$

7. Chromates fused in a bead of borax or of microcosmic salt impart a yellowish-green color to the bead while hot, which becomes emerald-green on cooling.

THIRD GROUP.

Acids which are not precipitated by $BaCl_2$, barium chloride, but are precipitated by $AgNO_3$, argentic nitrate : **Hydrochloric Acid, Hydrobromic Acid, Hydriodic Acid, Hydrocyanic Acid, Hydroferrocyanic Acid, Hydroferricyanic Acid, Sulphydric Acid (Hydrogen Sulphide), Nitrous Acid, Hypochlorous Acid.**

HYDROCHLORIC ACID, HCl.

(Hydrochloric acid combines with bases to form salts called chlorides.)

NaCl, sodium chloride, may be employed in making the tests.

1. The chlorides are soluble in water, with the exception of argentic chloride, mercurous chloride, and plumbic chloride; the latter, however, being sparingly soluble in cold water. (For dissolving insoluble chlorides, see Dissolving Oxides and Salts, page 104.)

2. $AgNO_3$, argentic nitrate, precipitates white, curdy AgCl, argentic chloride, insoluble in dilute nitric acid, easily soluble in ammonium hydroxide. From its solution in ammonium hydroxide the argentic chloride is reprecipitated by nitric acid. The precipitate is also soluble in KCN, potassium cyanide, and in $Na_2S_2O_3$, sodium hyposulphite. When exposed to sunlight the precipitate changes in color to violet and then to black.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates, in hydrochloric acid and in solutions of chlorides, white, sometimes crystalline $PbCl_2$, plumbic chloride, sparingly soluble in cold water, easily soluble in hot water, from which, when in concentrated solution, it crystallizes, on cooling, in glistening rhombic needles. Precipitation does not occur in very dilute solutions of chlorides.

4. On placing a dry mixture of a chloride and potassium bichromate in a small retort or tubulated fractionating flask, adding concentrated sulphuric acid, and carefully distilling the contents of the retort, CrO_2Cl_2, chlorochromic anhydride, as a brownish-red gas,[1] is produced, which, when conducted into a receiving flask, condenses into a brownish-red liquid:

$$4KCl + K_2Cr_2O_7 + 6H_2SO_4 = 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O.$$

Sodium hydroxide added to the brownish-red distillate produces a yellowish solution of Na_2CrO_4, sodium chromate[2] (together with sodium chloride):

$$CrO_2Cl_2 + 4NaOH = Na_2CrO_4 + 2NaCl + 2H_2O.$$

If the yellowish solution is acidified with acetic acid and plumbic acetate added, the production of a yellow precipitate of plumbic chromate gives indirect but conclusive evidence of chlorine.

HYDROBROMIC ACID, HBr.

(Hydrobromic acid combines with bases to form salts called bromides.)

KBr, potassium bromide, may be employed in making the tests.

1. The bromides in general are soluble in water. Argentic bromide and mercurous bromide are insoluble; plumbic bromide is sparingly soluble in water.

2. $AgNO_3$, argentic nitrate, precipitates yellowish-white, curdy AgBr, argentic bromide, insoluble in dilute nitric acid, sparingly soluble in dilute and more easily soluble in concentrated ammonium hydroxide. The precipitate is easily soluble in potassium cyanide and in sodium hyposulphite.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates in hydro-

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[1] Distinction from iodides, which furnish violet-colored vapors of free iodine.

[2] Distinction from bromides, which do not impart a color to the liquid.

bromic acid and in solutions of bromides white, crystalline $PbBr_2$, plumbic bromide, sparingly soluble in cold water, more easily soluble in hot water.

4. Dry bromides, on being distilled in a retort with potassium bichromate and concentrated sulphuric acid (see under Chlorides, 4, page 74), yield brown vapors of bromine, which condense in the receiver as a brown distillate of bromine, free from chromium:

$$6KBr + K_2Cr_2O_7 + 7H_2SO_4 = Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + Br_6.$$

Sodium hydroxide added to the distillate decolorizes it, forming sodium bromide and NaBrO, sodium hypobromite:

$$Br_2 + 2NaOH = NaBr + NaBrO + H_2O.$$

5. Chlorine-water added in small quantity to a solution of a bromide liberates bromine, which remains dissolved in the water. On adding a small quantity of chloroform or of carbon disulphide (both of which are insoluble in water and sink to the bottom of the test-tube), closing the mouth of the tube with the thumb, and thoroughly shaking it, the chloroform or carbon disulphide extracts the bromine and collects at the bottom of the tube as a yellowish or brownish liquid. The depth of coloration depends upon the quantity of bromine present.

If an excess of chlorine-water is used, decolorization of the liquid occurs, due to the formation of $HBrO_3$, bromic acid:

$$Br_2 + Cl_{10} = 2BrCl_5;$$
$$BrCl_5 + 3H_2O = HBrO_3 + 5HCl.$$

HYDRIODIC ACID, HI.

(Hydriodic acid combines with bases to form salts called iodides.)

KI, potassium iodide, may be employed in making the tests.

1. Most of the iodides are soluble in water; the others are soluble in acids, with the exception of argentic iodide. Plumbic iodide is sparingly soluble in cold water.

2. $AgNO_3$, argentic nitrate, precipitates yellowish, amorphous AgI, argentic iodide, insoluble in nitric acid and in ammonium hydroxide, soluble in potassium cyanide and in sodium hyposulphite.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates in solutions of hydriodic acid and of iodides yellow, crystalline PbI_2, plumbic iodide, soluble in hot water, from which, on cooling, it separates in glistening yellow, six-sided plates.

4. Dry iodides, distilled in a retort with potassium bichromate and concentrated sulphuric acid (see under Chlorides, 4, page 74), yield violet vapors of iodine:[1]

$$6KI + K_2Cr_2O_7 + 7H_2SO_4 = Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + I_6.$$

The iodine contained in the distillate is soluble in sodium hydroxide, forming NaI, sodium iodide, and $NaIO_3$, sodium iodate, the distillate at the same time becoming colorless:

$$I_6 + 6NaOH = 5NaI + NaIO_3 + 3H_2O.$$

5. Chlorine-water added in small quantity to a solution of an iodide liberates iodine, which imparts a yellowish or brownish-yellow color to the solution. On adding a small quantity of chloroform or of carbon disulphide to the liquid, closing the tube with the thumb, and thoroughly shaking it, the chloroform or carbon disulphide will settle at the bottom of the tube, and be found to possess a blue color, due to the free iodine extracted from the aqueous solution.

If, instead of chloroform or carbon disulphide, a drop of dilute starch paste is added, the solution becomes blue, due to the action of the free iodine upon the starch. The test is exceedingly delicate, and when considerable iodine is present

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[1] Distinction from chlorine and bromine.

the liquid becomes black upon the addition of the starch; therefore strong solutions of iodides should be diluted before making this test.

The addition of an excess of chlorine-water causes the oxidation of the iodine to iodic acid, with a consequent decolorization of the liquid:

$$I_2 + Cl_{10} = 2ICl_5;$$
$$ICl_5 + 3H_2O = HIO_3 + 5HCl.$$

HYDROCYANIC ACID, HCN.

(Hydrocyanic acid combines with bases to form salts called cyanides.)

KCN, potassium cyanide, may be employed in making the tests.

1. Of the cyanides those of the alkalies and of the alkaline earths are soluble in water (also mercuric cyanide); the cyanides of the heavy metals are insoluble in water, although many of them are soluble in potassium cyanide, with the formation of double salts; for example:

$$AgCN + KCN = AgCN\,KCN.$$

By the addition of an acid to these solutions, the cyanide of the heavy metal is usually but not invariably reprecipitated, with the evolution of hydrocyanic acid:

$$AgCN\,KCN + HNO_3 = AgCN + HCN + KNO_3.$$

For methods of dissolving and fusing cyanides, see 4, page 111.

2. $AgNO_3$, argentic nitrate, precipitates in solutions of hydrocyanic acid and of cyanides white, curdy AgCN, insoluble in nitric acid, easily soluble in ammonium hydroxide. From this solution it is reprecipitated by nitric acid:

$$AgCN + NH_3 = NH_3AgCN;$$
$$NH_3AgCN + HNO_3 = AgCN + NH_4NO_3.$$

Argentic cyanide is soluble in potassium cyanide; therefore

a precipitate appears only after an excess of argentic nitrate has been added. It is also soluble in sodium hyposulphite. On igniting argentic cyanide it breaks up into metallic silver and cyanogen gas (together with some argentic paracyanide):

$$AgCN = Ag + CN.$$

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, produces in solutions of cyanides a white precipitate of $Pb(CN)_2$, plumbic cyanide, soluble in nitric acid.

4. If NaOH, sodium hydroxide, $FeSO_4$, ferrous sulphate, and Fe_2Cl_6, ferric chloride, are added in small quantities to a solution of hydrocyanic acid or to a cyanide, the mixture warmed, and finally acidulated with hydrochloric acid, a blue precipitate of $Fe_4(Fe(CN)_6)_3$, ferric ferrocyanide (Prussian blue), is formed; while the ferrous hydroxide first produced is dissolved by the acid. The ferrous sulphate with the sodium hydroxide produces $Fe(OH)_2$, ferrous hydroxide:

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4,$$

which, on being warmed with the cyanide solution, yields a ferrocyanide; for example, with potassium cyanide it yields $K_4Fe(CN)_6$, potassium ferrocyanide:

$$Fe(OH)_2 + 6KCN = K_4Fe(CN)_6 + 2KOH,$$

which combines with the iron of the ferric chloride to form blue ferric ferrocyanide (Prussian blue).

5. To detect hydrocyanic acid which is being evolved from a liquid, a drop of yellow ammonium sulphide and of ammonium hydroxide is placed on the concave side of a watch-glass, the watch-glass inverted and placed as a cover over the vessel in which the hydrocyanic acid is being evolved, so that the vapors of the acid coming in contact with the ammoniacal liquid can be absorbed. After some time the watch-glass is removed, placed on a water-bath, and warmed, whereby NH_4CNS, ammonium sulphocyanide, is produced:

$$HCN + (NH_4)_2S_2 + NH_4OH = NH_4CNS + (NH_4)_2S + H_2O,$$

which remains as a dry residue on the complete evaporation of the liquid. This residue is dissolved in a little water; a few drops of hydrochloric acid (to decompose any $(NH_4)_2S$ remaining) and a drop of ferric chloride are added, whereby a claret-red coloration is produced, due to the formation of $Fe_2(CNS)_6$, ferric sulphocyanide.

6. When heated in a reduction-tube the cyanides of the heavy metals are decomposed; the cyanides of the noble metals break up into metal and cyanogen gas; other cyanides break up into metal, carbon, and nitrogen. Argentic and mercuric cyanides, in which the cyanogen cannot be detected by the ordinary reagents, can be recognized in this manner. Mercuric cyanide in aqueous solutions, when treated with hydrogen sulphide, decomposes and forms mercuric sulphide and hydrocyanic acid. HCN and CN are virulent poisons.

HYDROFERROCYANIC ACID, $H_4Fe(CN)_6$.

(Hydroferrocyanic acid combines with bases to form salts called ferrocyanides.)

$K_4Fe(CN)_6$, potassium ferrocyanide, may be employed in making the tests.

1. The ferrocyanides, with the exception of those of the alkalies and of the alkaline earths, are mostly insoluble in water. Regarding their solution and fusion, see page 112.

2. $AgNO_3$, argentic nitrate, precipitates white $Ag_4Fe(CN)_6$, argentic ferrocyanide, insoluble in nitric acid and in ammonium hydroxide, soluble in potassium cyanide.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, in solutions of ferrocyanides precipitates white $Pb_2Fe(CN)_6$, plumbic ferrocyanide, insoluble in dilute nitric acid.

4. Ferrous salts ($FeSO_4$, ferrous sulphate) produce in solutions of ferrocyanides (when the ferrocyanide is in excess) a

white precipitate, which, on exposure to the air, rapidly changes to bluish-white $K_2Fe(Fe(CN)_6)$, potassium ferrous ferrocyanide (Everett's salt). When the ferrous salt is in excess, $Fe_2Fe(CN)_6$, ferrous ferrocyanide, is produced.

5. Ferric salts (Fe_2Cl_6, ferric chloride) precipitate dark-blue $Fe_4(Fe(CN)_6)_3$, ferric ferrocyanide (Prussian blue), insoluble in acids.

6. $CuSO_4$, cupric sulphate, precipitates brownish-red $Cu_2Fe(CN)_6$, cupric ferrocyanide.

HYDROFERRICYANIC ACID, $H_3Fe(CN)_6$.

(Hydroferricyanic acid combines with bases to form salts called ferricyanides.)

$K_3Fe(CN)_6$, potassium ferricyanide, may be employed in making the tests.

1. Of the ferricyanides those of the alkalies and of the alkaline earths are soluble in water, while those of the heavy metals are mostly insoluble in water. Regarding their solution and fusion, see page 112.

2. $AgNO_3$, argentic nitrate, precipitates from solutions of ferricyanides reddish-brown $Ag_3Fe(CN)_6$, argentic ferricyanide, insoluble in nitric acid, soluble in ammonium hydroxide and in potassium cyanide.

3. Ferrous salts ($FeSO_4$, ferrous sulphate) precipitate $Fe_3(Fe(CN)_6)_2$, ferrous ferricyanide (Turnbull's blue), insoluble in acids. Ferric salts fail to produce a precipitate, but cause a dark coloration; possibly soluble $Fe_2(Fe(CN)_6)_2$, ferric ferricyanide, is produced:

$$Fe_2Cl_6 + 2K_3Fe(CN)_6 = Fe_2(Fe(CN)_6)_2 + 6KCl.$$

4. $CuSO_4$, cupric sulphate, precipitates greenish-yellow $Cu_3(Fe(CN)_6)_2$, cupric ferricyanide.

SULPHYDRIC ACID, H_2S (HYDROGEN SULPHIDE).

(Sulphydric acid combines with bases to form salts called sulphides.)

Na_2S, sodium sulphide, may be employed in making the tests.

1. The sulphides, with the exception of those of the alkalies and of the alkaline earths, are insoluble in water. Most of them are soluble in hydrochloric and in nitric acids; some are soluble only in nitro-hydrochloric acid. (See Sulphides of the Heavy Metals, page 111.) They may be recognized by their giving off hydrogen sulphide when dissolved in hydrochloric acid, or by the separation of sulphur when dissolved in nitric acid or in nitro-hydrochloric acid.

2. $AgNO_3$, argentic nitrate, precipitates black Ag_2S, argentic sulphide, soluble in nitric acid when warmed.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates in solutions of sulphides or of hydrogen sulphide black PbS, plumbic sulphide, soluble in nitric acid when warmed.

4. To detect hydrogen sulphide gas a strip of filter-paper is moistened with plumbic acetate and held in the atmosphere containing the gas. In the presence of hydrogen sulphide the paper becomes brown or black, due to the formation of PbS, plumbic sulphide.

5. A few drops of an alkaline solution of plumbic oxide ($Pb(OK)_2$, potassium plumbite), added to a solution containing hydrogen sulphide or a sulphide of a metal, produces a perceptible brownish coloration, even if only the slightest trace of the sulphide be present.

6. $Na_2NOFe(CN)_5$, sodium nitro-prusside, solutions are colored violet by sulphides, but not by solutions of free hydrogen sulphide.

7. Many of the sulphides of the metals, when heated in a reduction-tube, yield a sublimate of sulphur. Sulphides,

heated in a glass tube open at both ends and held obliquely in the flame, are oxidized, with the formation of SO_2, sulphurous anhydride. Ignited with sodium carbonate in the reducing flame on charcoal, they yield sodium sulphide, which, when placed on a clean silver coin and moistened with water, produces a black discoloration of argentic sulphide.

NITROUS ACID, HNO_2.

(Nitrous acid combines with bases to form salts called nitrites.)

KNO_2, potassium nitrite, may be employed in making the tests.

1. Most of the nitrites are soluble in water. Treated with hydrochloric or sulphuric acid they evolve brownish-red fumes of NO_2, nitrogen dioxide.

2. $AgNO_3$, argentic nitrate, precipitates white $AgNO_2$, argentic nitrite, soluble with difficulty in water.

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, colors solutions of nitrous acid yellow.

4. H_2S, hydrogen sulphide, is decomposed by nitrous acid with the separation of sulphur:

$$H_2S + 2HNO_2 = 2NO + S + 2H_2O.$$

5. $FeSO_4$, ferrous sulphate, added to a solution of a nitrite containing a few drops of sulphuric acid,[1] produces a brown or black coloration, due to the formation of NO, nitrogen monoxide, which enters into combination with the ferrous sulphate:

$$(x+3)FeSO_4 + H_2SO_4 + 2HNO_2 = xFeSO_4(NO)_2 + Fe_2(SO_4)_3 + 2H_2O.$$

Heating the liquid causes the coloration to disappear.

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[1] The nitrites of commerce usually contain free nitrous acid, and therefore respond to the test without the addition of sulphuric acid.

6. KI, potassium iodide, (or CdI_2, cadmium iodide,) starch paste, and dilute sulphuric acid, added to a solution of a nitrite, immediately produce a blue coloration in the liquid. The nitrous acid liberates iodine from the hydriodic acid:

$$2HNO_2 + 2HI = 2NO + 2H_2O + I_2.$$

The free iodine combining with the starch forms the blue compound. (In this test cadmium iodide or potassium iodide free from iodic acid should be used, as hydriodic and iodic acid undergo decomposition when together, with the liberation of iodine:

$$5HI + HIO_3 = I_6 + 3H_2O.)$$

HYPOCHLOROUS ACID, HClO.

(Hypochlorous acid combines with bases to form salts called hypochlorites.)

NaClO, sodium hypochlorite, may be employed in making the tests.

1. The hypochlorites, as a rule, contain chlorides, produced, during the preparation of the hypochlorite, by the action of the chlorine upon hydroxides:

$$2NaOH + Cl_2 = NaClO + NaCl + H_2O.$$

On the addition of acids they are decomposed, with the evolution of chlorine:

$$NaClO + 2HCl = NaCl + Cl_2 + H_2O;$$
$$NaClO + NaCl + H_2SO_4 = Na_2SO_4 + Cl_2 + H_2O.$$

2. $AgNO_3$, argentic nitrate, added to a solution of a hypochlorite produces soluble AgClO, argentic hypochlorite, which immediately breaks up into white, insoluble AgCl, argentic chloride, and soluble $AgClO_3$, argentic chlorate:

$$6AgClO = 2AgClO_3 + 4AgCl.$$

3. $Pb(C_2H_3O_2)_2$, plumbic acetate, produces at first a white precipitate of $PbCl_2$, plumbic chloride, which soon becomes

yellow and finally brown, due to the formation of PbO_2, lead dioxide. (In like manner $MnSO_4$, manganous sulphate, yields brown $MnO(OH)_2$, hydrated peroxide of manganese.)

FOURTH GROUP.

Acids which are not precipitated by barium chloride or by argentic nitrate: **Nitric Acid, Chloric Acid.**

NITRIC ACID, HNO_3.

(Nitric acid combines with bases to form salts called nitrates.)

KNO_3, potassium nitrate, may be employed in making the tests.

1. The nitrates, with the exception of a few basic salts, are soluble in water. Some nitrates (for example, $Ba(NO_3)_2$, barium nitrate) are only sparingly soluble in nitric acid.

2. $BaCl_2$, $Pb(C_2H_3O_2)_2$, and $AgNO_3$ do not produce precipitates in solutions of nitrates.

3. On placing a small crystal of $FeSO_4$, ferrous sulphate, in a cooled mixture of concentrated sulphuric acid and a solution of a nitrate, a brownish-black ring is formed around the crystal. In the reduction of the nitric acid NO, nitrogen monoxide, is produced, which combines with the ferrous sulphate to form an unstable compound:

$$(x+6)FeSO_4 + 3H_2SO_4 + 2HNO_3 = [xFeSO_4(NO)_2] + 3Fe_2(SO_4)_3 + 4H_2O.$$

The test is best made in a flat porcelain dish, or in a watch-glass placed on white paper. Heat destroys the black ring.

4. KI, potassium iodide, (or CdI_2, cadmium iodide,) starch paste, and dilute sulphuric acid, added to a solution of a nitrate, produce no reaction (distinction from nitrites), but,

on placing a fragment of zinc in the liquid, nitrous acid is evolved, which, acting upon the potassium iodide, liberates the iodine, which with the starch produces a blue coloration:

$$HNO_3 + Zn + H_2SO_4 = HNO_2 + ZnSO_4 + H_2O;$$
$$2HNO_2 + 2HI = 2NO + 2H_2O + I_2.$$

5. Nitrates of the alkalies when heated in a reduction-tube are reduced to nitrites, with the evolution of oxygen:

$$KNO_3 = KNO_2 + O.$$

The nitrates of the heavy metals when heated in a reduction-tube evolve reddish-brown fumes of nitrogen dioxide:

$$Pb(NO_3)_2 = PbO + O + 2NO_2.$$

The latter reaction also takes place when a nitrate of an alkali mixed with cupric sulphate is heated in a reduction-tube:

$$2KNO_3 + CuSO_4 = K_2SO_4 + CuO + O + 2NO_2.$$

Nitrates deflagrate when ignited on charcoal.

CHLORIC ACID, $HClO_3$.

(Chloric acid combines with bases to form salts called chlorates.)

$KClO_3$, potassium chlorate, may be employed in making the tests.

1. The chlorates are soluble in water.

2. $BaCl_2$, barium chloride, does not produce a precipitate in solutions of chlorates. $Pb(C_2H_3O_2)_2$, plumbic acetate, and $AgNO_3$, argentic nitrate, do not produce precipitates if the solution of the chlorate be free from chlorides.

3. On warming a solution of a chlorate with hydrochloric acid the liquid becomes greenish yellow in color, and greenish-yellow fumes of a mixture of chlorine and Cl_2O_4, chlorine tetroxide (chlorine peroxide), are evolved:

$$KClO_3 + 6HCl = KCl + Cl_6 + 3H_2O;$$
$$2KClO_3 + 4HCl = 2KCl + Cl_2O_4 + Cl_2 + 2H_2O.$$

4. Concentrated sulphuric acid poured over a *very small* piece of a chlorate in a porcelain dish causes a decomposition of the chlorate, with the production of a perchlorate and chlorine tetroxide (chlorine peroxide):

$$3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + Cl_2O_4 + H_2O.$$

Great care should be used in making this test, and only small quantities of chlorate should be employed. Warming should be avoided, as explosions, which may cause personal injury, are likely to occur on the application of heat.

5. Chlorates heated in a reduction-tube undergo decomposition, and are converted into chlorides, with the evolution of oxygen:

$$KClO_3 = KCl + O_3.$$

(Bromates and iodates undergo a similar decomposition on being heated, forming respectively bromides and iodides, with the evolution of oxygen.)

APPENDIX: ORGANIC ACIDS.

Acetic Acid, Oxalic Acid, Tartaric Acid.

ACETIC ACID, $HC_2H_3O_2$.

(Acetic acid combines with bases to form salts called acetates.)

$NaC_2H_3O_2$, sodium acetate, may be employed in making the tests.

1. Most of the acetates are easily soluble in water.

2. $BaCl_2$, barium chloride, and $Pb(C_2H_3O_2)_2$, plumbic acetate, do not produce precipitates in solutions of acetates.

3. $AgNO_3$ argentic nitrate, precipitates, in concentrated acetic acid or in concentrated solutions of acetates, crystalline $AgC_2H_3O_2$, argentic acetate, soluble in a large quantity of water and in ammonium hydroxide.

4. Fe_2Cl_6, ferric chloride, added to a neutral acetate, or to acetic acid, which must afterwards be exactly neutralized with ammonium hydroxide, produces a reddish-brown solution of $Fe_2(C_2H_3O_2)_6$, ferric acetate:

$$6NaC_2H_3O_2 + Fe_2Cl_6 = Fe_2(C_2H_3O_2)_6 + 6NaCl.$$

On warming this solution a precipitate of brownish-red $Fe_2(OH)_4(C_2H_3O_2)_2$, basic ferric acetate, separates, while the supernatant liquid becomes colorless:

$$Fe_2(C_2H_3O_2)_6 + 4H_2O = Fe_2(OH)_4(C_2H_3O_2)_2 + 4HC_2H_3O_2.$$

5. On adding sulphuric acid to a solution of an acetate and warming the liquid, $HC_2H_3O_2$, acetic acid, is liberated, which may be recognized by its odor of vinegar.

6. On adding C_2H_5OH, alcohol, to a cool solution of an acetate containing sulphuric acid and then warming the liquid, $C_2H_5C_2H_3O_2$, ethyl acetate (acetic ether), is produced, which may be recognized by its characteristic apple-like odor:

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O;$$

$$C_2H_5HSO_4 + HC_2H_3O_2 = C_2H_5C_2H_3O_2 + H_2SO_4.$$

The alcohol should not be added while the liquid is hot, as violent ebullition might occur with consequent spurting of the liquid.

7. Acetates on being ignited are decomposed, without the separation of carbon, into volatile products (for example, acetone) and carbonates or oxides of the metals which were in combination as acetates.

OXALIC ACID, $H_2C_2O_4$.

(Oxalic acid combines with bases to form salts called oxalates.)

$(NH_4)_2C_2O_4$, ammonium oxalate, may be employed in making the tests.

1. Of the oxalates those of the alkalies are soluble in water; most of the others are insoluble in water.

2. $BaCl_2$, barium chloride, precipitates in solutions of neutral oxalates white BaC_2O_4, barium oxalate, easily soluble in hydrochloric and in nitric acid.

3. $CaCl_2$, calcium chloride, precipitates from neutral solutions of oxalates white CaC_2O_4, calcium oxalate, soluble in hydrochloric and in nitric acid, insoluble in acetic acid.

4. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates white PbC_2O_4, plumbic oxalate, soluble in nitric acid.

5. $AgNO_3$, argentic nitrate, precipitates white $Ag_2C_2O_4$, argentic oxalate, soluble in nitric acid and in ammonium hydroxide.

6. Concentrated sulphuric acid, on being warmed with oxalic acid or oxalates, decomposes them into water, CO_2, carbon dioxide, and CO, carbon monoxide:

$$H_2C_2O_4 + H_2SO_4 = H_2O + CO_2 + CO + H_2SO_4.$$

On pouring the gases into a test-tube containing clear solution of calcium hydroxide (lime-water), closing the tube with the thumb, and shaking it, the production of a milky turbidity, due to the formation of calcium carbonate, indicates the presence of carbon dioxide.

7. Oxalates on ignition are decomposed into carbon monoxide and carbonates or oxides of the metals which were in combination as oxalates. Pure oxalates on being ignited do not become black in color:

$$K_2C_2O_4 = CO + K_2CO_3.$$

TARTARIC ACID, $H_2C_4H_4O_6$.

(Tartaric acid combines with bases to form salts called tartrates.)

$KNaC_4H_4O_6$, potassium sodium tartrate, may be employed in making the tests.

1. The tartrates of the alkalies and some of the tartrates

of the heavy metals are soluble in water, the other tartrates are soluble in acids.

2. $BaCl_2$, barium chloride, added in excess precipitates white $BaC_4H_4O_6$, barium tartrate, soluble in hydrochloric and in nitric acid.

3. $CaCl_2$, calcium chloride, added in excess precipitates white, crystalline $CaC_4H_4O_6$, calcium tartrate, soluble in hydrochloric, nitric, and acetic acids. The precipitate is also soluble in potassium or sodium hydroxides, forming a clear liquid, from which, on boiling, the calcium salt separates in gelatinous masses. Probably a salt, $CaNa_2C_4H_2O_6$, is produced in which the hydrogen atoms of the alcoholic hydroxyl of the tartaric acid have also been replaced by a metal:

$$CaC_4H_4O_6 + 2NaOH = CaNa_2C_4H_2O_6 + 2H_2O.$$

This compound, on being boiled with considerable water, is reconverted into the original calcium tartrate:

$$CaNa_2C_4H_2O_6 + 2H_2O = CaC_4H_4O_6 + 2NaOH.$$

4. $Pb(C_2H_3O_2)_2$, plumbic acetate, precipitates white $PbC_4H_4O_6$, plumbic tartrate, soluble in nitric acid and in ammonium hydroxide.

5. $AgNO_3$, argentic nitrate, precipitates in solutions of neutral tartrates $Ag_2C_4H_4O_6$, argentic tartrate, soluble in nitric acid and in ammonium hydroxide. On boiling the precipitate it is decomposed, with the separation of metallic silver.

6. Tartrates on being ignited are decomposed, with the production of an odor resembling burnt sugar, the separation of carbon and the formation of carbonates.

III. PRELIMINARY EXAMINATION.

(A) PRELIMINARY TESTS IN THE DRY WAY.

The special tests for bases and acids (testing in the Wet Way) are always preceded by a short preliminary examination (in the Dry Way), in order to obtain general information regarding the nature of the substance to be analyzed. It is hardly possible to determine the best method to be employed in the preparation of the substance for analysis without resorting to this preliminary examination. It should therefore never be omitted.

When solutions are to be analyzed, a portion is evaporated to dryness at a moderate temperature (without ignition), and the residue used for the preliminary tests.

1. EXAMINATION IN THE REDUCTION-TUBE.

To ascertain the behavior of the substance at higher temperatures, a small portion of it, or of the residue obtained by evaporation, is placed in a narrow glass tube closed at one end, and heated, at first slightly, afterwards more strongly, and then to redness.

The occurrence of any of the following changes should especially be noted:

1. *Separation of Carbon:* Indicates the presence of organic compounds. Simultaneously a generation of empyreumatic vapors takes place, or, if nitrogen is present, an odor of burnt feathers.

2. *Elimination of Water:* Indicates the presence of water of crystallization or of adherent moisture; frequently a

change of color occurs, as in the transformation of the blue hydrous sulphate of copper ($CuSO_4 + 5H_2O$) into the anhydrous salt ($CuSO_4$). Intumescence may take place as in the case of borax ($Na_2B_4O_7 + 10H_2O$), or decrepitation as in sodium chloride (in consequence of the violent expulsion of water confined between the lamellæ of the crystals).

3. *Change in Color:* Indicates the presence of combinations of heavy metals. The change may be caused by the elimination of water (see 2, page 90), or by the conversion of salts into oxides; for example, cupric nitrate and cupric carbonate become black in color when heated, due to their conversion into cupric oxide:

$$Cu(NO_3)_2 = CuO + 2NO_2 + O;$$
$$CuCO_3 = CuO + CO_2.$$

Many compounds differ in color when hot and when cold; for example, oxide of zinc is yellow when hot and white when cold.

4. *Formation of a Sublimate:* Indicates the presence of volatile compounds.

(*a*) White sublimate: Salts of mercury, ammonium salts, arsenious oxide, antimonious oxide.—On heating the sublimate with dry sodium carbonate, salts of mercury become red, due to the formation of mercuric oxide (frequently metallic mercury is produced at the same time); for example:

$$HgCl_2 + Na_2CO_3 = HgO + CO_2 + 2NaCl.$$

Ammonium salts evolve ammoniacal gas, which may be recognized by the odor, and by its coloring moistened turmeric-paper brown, and red litmus-paper blue:

$$2NH_4Cl + Na_2CO_3 = 2NH_3 + CO_2 + H_2O + 2NaCl.$$

Arsenical vapors and antimonious oxide are apparently not changed when heated with sodium carbonate. The arsenic sublimes in octahedral crystals; the antimony forms an amorphous sublimate, which sometimes contains crystals.

(*b*) Yellow sublimate: Mercuric iodide (becomes red when stirred), arsenious sulphide.

(*c*) Yellow to red: Compounds of mercury (formation of basic salts).

(*d*) Yellow to brownish yellow: Sulphur (when hot collects in reddish-brown drops). Free sulphur, or sulphides rich in sulphur,—for example, $Sb_2S_5 = Sb_2S_3 + S_2$.

(*e*) Gray to black: Mercury (globules); mercuric sulphide (black, red when rubbed); iodine (violet vapors, characteristic odor of iodine); arsenic (mirror).

It is to be remembered that, in addition to the sublimates mentioned, quite a number of compounds exist which are more or less volatile,—for example, many chlorides.

5. *Evolution of Vapors:*

(*a*) Colorless vapors should be tested for their reaction with litmus-paper. The acids frequently form clouds when escaping from the tube (in consequence of their changing from the anhydrous to the hydrous state).

(*b*) Reddish-brown vapors: Nitrogen dioxide, bromine. Nitrogen dioxide, resulting from the decomposition of nitrates of the heavy metals,—for example, $Pb(NO_3)_2 = PbO + 2NO_2 + O$,—does not color starch-paper, and is recognized by its odor. Bromine, also recognizable by its odor, colors starch-paper reddish yellow.

(*c*) Violet vapors: Iodine. Characteristic odor; frequently simultaneous formation of a black sublimate. Colors starch-paper blue to brownish black.

6. *Production of an Odor:*

(*a*) Odor of ammonia: Ammonium salts; compounds of cyanogen or organic compounds containing nitrogen.

(*b*) Odor of sulphurous anhydride: Resulting from the decomposition of sulphates.

(*c*) Odor of cyanogen: Compounds of cyanogen. Cyan-

ogen gas burns when ignited, with a flame pinkish lavender in color:

$$CN + O_2 = CO_2 + N.$$

(*d*) Odor of garlic: Compounds of arsenic, resulting from reduction.

7. *Evolution of Oxygen* (may be recognized by the flaring or re-igniting of a glowing stick held at the mouth of the tube): Indicates the presence of peroxides,—for example, pyrolusite, MnO_2:

$$3MnO_2 = Mn_3O_4 + O_2;$$

of mercuric oxide:

$$HgO = Hg + O;$$

of salts rich in oxygen,—for example:

$$KClO_3 = KCl + O_3.$$

2. EXAMINATION ON CHARCOAL.

To determine the behavior of substances in the reducing flame a small portion of the substance, generally mixed with dry sodium carbonate, is heated in a cavity in the charcoal by means of the reducing flame of the blowpipe.[1] The sodium carbonate is added in order to transform salts and sulphates into carbonates and oxides respectively,—for example:

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4;$$

$$CuCl_2 + Na_2CO_3 = CuO + CO_2 + 2NaCl.$$

The addition of sodium carbonate is not necessary in the case of metals that form metallic globules, oxides, and salts which are easily decomposed, as the alkalies and their salts are absorbed by the charcoal (because of their easy fusibility). The

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[1] The reducing flame is obtained by holding the blowpipe near the flame and by gentle blowing directing it upon the substance to be heated. The oxidizing flame is obtained by placing the blowpipe in the interior of the flame and blowing with force.

oxides of the remaining elements may be recognized by the following characteristics:

1. *The oxides of the heavy metals* heated in the reducing flame are reduced by the charcoal. The metals themselves are either volatile or non-volatile, may oxidize or not, and may be fusible or infusible; therefore fused globules may be obtained, or infusible masses and incrustations, the latter resulting from the presence of metals that volatilize and oxidize. From plumbic oxide, for example, metallic lead is obtained:

$$PbO + C = Pb + CO,$$

part of which volatilizes, combines with the oxygen of the air, and is deposited on the cooler part of the charcoal as an incrustation of yellow oxide:

$$Pb + O = PbO.$$

The metallic globules differ in their behavior in the oxidizing flame: some change into oxides and others remain unchanged. The ductility should also be ascertained; for this purpose the globule is placed in a mortar and struck with the pestle; those which are ductile are flattened into plates, while those which are brittle break into pieces and may be pulverized by subsequent rubbing.

(*a*) Fused metallic globules, without incrustation, are produced:

Yellow: gold, ductile, not oxidizable.
White: silver, ductile, not oxidizable.
Red: copper,[1] ductile, oxidizable.

With incrustation,—White globule, incrustation yellow:

Ductile: lead, oxidizable.
Brittle: bismuth, oxidizable.

White globule, incrustation white:

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[1] Generally obtained as metallic spangles.

Ductile: tin,[1] oxidizable.

Brittle: antimony, oxidizable.

(*b*) Incrustation without metallic globule:

White (when hot, yellow when cold): zinc.

Yellowish red to brown: cadmium.

(*c*) Gray, infusible masses:

$\left.\begin{array}{l}\text{Iron}\\\text{Cobalt}\\\text{Nickel}\\\text{Manganese}\end{array}\right\}$ oxidizable.

Platinum: not oxidizable.

(*d*) Neither globule nor incrustation:

Volatile with odor of garlic: arsenic.

Volatile without odor of garlic: mercury.

In examining metallic globules it is to be remembered that in the presence of different metals alloys may be formed.

2. *White infusible masses* remain on the charcoal if salts of the alkaline earths, magnesium or aluminium, are present. (By the action of Na_2CO_3, carbonates and oxides are formed.) The white masses, moistened with a solution of cobaltous nitrate and strongly heated in the oxidizing flame, yield as follows:

Aluminium: blue masses (infusible).

Magnesium: pink-colored masses.

$\left.\begin{array}{l}\text{Barium}\\\text{Strontium}\\\text{Calcium}\end{array}\right\}$ gray masses.

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[1] Tin and antimony are obtained with difficulty in the form of globules when sodium carbonate is employed. Therefore on the appearance of a white incrustation a second test is made, in which, in addition to sodium carbonate, potassium cyanide is added to the salt, and the whole heated in the reducing flame. (KCN thereby changes into KCNO: for example, $SnO_2 + 2KCN = Sn + 2KCNO$.) Compare also its behavior with cobalt solution, see 6, page 34.

The cobaltous nitrate on being heated is converted into cobaltous oxide:

$$Co(NO_3)_2 = CoO + 2NO_2 + O,$$

which combines with aluminium and magnesium compounds. With barium, strontium, and calcium, mixtures only of the oxides are obtained.

Many silicates and phosphates which are fusible with difficulty, and also many borates and arseniates, may form blue masses when ignited with cobaltous nitrate; frequently these double salts of cobalt are easily fusible.

Zinc oxide, when ignited with cobaltous nitrate, becomes yellowish green in color; antimonious oxide, a dirty green; stannic oxide, bluish green. (Compounds of CoO are produced with the different oxides.)

3. *Green fused masses* (consisting of chromic oxide) indicate salts of chromium and chromates.

4. *Yellow or brown fused masses*, consisting of sodium sulphide, indicate the presence of compounds containing sulphur. A portion is placed on a silver coin and moistened with water to ascertain whether a black discoloration of Ag_2S is produced. (See 7, page 81.) As the formation of sodium sulphide by the reduction of salts containing acids of sulphur requires time, and, like all alkali compounds, the sulphide impregnates the charcoal on continued heating, these tests must be made just after the reduction has taken place and before the sodium sulphide has been absorbed by the charcoal.

Many of the compounds containing sulphur,—for example, the sulphides,—when heated in a small glass tube open at both ends and held obliquely in the flame, yield sulphurous anhydride, which is easily recognized by its odor.

3. EXAMINATION BY MEANS OF MICROCOSMIC SALT.

A portion of sodium ammonium phosphate (microcosmic salt) is heated in a loop of platinum wire until it melts, and forms a bead. A very small portion of the substance to be examined is then attached to the clear bead, which is again heated in the oxidizing flame or in the oxidizing space of a Bunsen flame. The $NaNH_4HPO_4 + 4H_2O$, sodium ammonium phosphate, when fused, first loses its water of crystallization and then changes into sodium metaphosphate:

$$NaNH_4HPO_4 = NaPO_3 + H_2O + NH_3.$$

The sodium metaphosphate dissolves most of the oxides and salts (in the latter a replacement of the acids takes place), and forms beads, generally characteristic in color:

$$CuO + NaPO_3 = CuNaPO_4;$$

$$CuSO_4 + NaPO_3 = CuNaPO_4 + SO_3.$$

Some of the beads change color in the reducing flame or in the reducing space of the Bunsen flame (in consequence of the reduction of the phosphates); for example, the transparent bluish-green copper bead by reduction becomes brownish-red and opaque:

$$CuNaPO_4 + C = NaPO_3 + Cu + CO;$$

the violet manganic oxide bead in the reducing flame is converted into the colorless manganous bead:

$$Mn_2(NaPO_4)_3 + C = 2MnNaPO_4 + NaPO_3 + CO.$$

Borax ($Na_2B_4O_7 + 10H_2O$) with oxides and salts yields beads similar to microcosmic salt, which are likewise reducible:

$$Na_2B_4O_7 + CuO = 2NaBO_2 + Cu(BO_2)_2;$$

$$Na_2B_4O_7 + CuSO_4 = 2NaBO_2 + Cu(BO_2)_2 + SO_3;$$

$$2NaBO_2 + Cu(BO_2)_2 + C = Na_2B_4O_7 + Cu + CO.$$

The reduction of the oxide in the beads is often facilitated by adding a small piece of tin foil:

$$2CuNaPO_4 + Sn = Sn(NaPO_4)_2 + Cu_2.$$

The following elements[1] produce characteristic colorations in the bead of microcosmic salt:

	Oxidizing Flame.	*Reducing Flame.*
Iron:	yellow to dark red when hot, light yellow to colorless when cold.	Green to colorless.
Nickel:	same as iron.	As in the oxidizing flame.[2]
Cobalt:	blue.	Blue.
Manganese:	violet.	Colorless.
Chromium:	green.	Green.
Copper:	blue-green.	Brownish, opaque.

The remaining oxides yield colorless, transparent or translucent, enamel-like beads.

The behavior of silicic acid and of the silicates in the bead of microcosmic salt is characteristic. Silicic acid does not dissolve in the bead, but, while the bead is in a state of fusion, swims in distinctly outlined masses. The silicates are decomposed in the bead, with the separation of undissolved silicic acid:

$$NaPO_3 + CaSiO_3 = CaNaPO_4 + SiO_2.$$

4. EXAMINATION IN THE FLAME.

If the presence of alkalies or alkaline earths is suspected, a small portion of the substance, or of the residue obtained by evaporation, is attached to a loop of *clean* platinum wire,[3] moistened with a drop of hydrochloric acid, and held in the flame of a Bunsen burner.

The flame is colored by the salts of

Potassium: violet.

Sodium: intense yellow.

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[1] For beads produced by the rare elements, see Appendix.

[2] For the behavior of nickel in the borax bead, see 7, page 49.

[3] Or the wire may be dipped in the concentrated solution of the substance to be examined.

Barium: green.
Strontium: crimson.
Calcium: yellowish red.

It must be remembered that, if two or more of these elements are present, one colored flame may interfere with the other.

Salts of copper and also boric acid color the flame green. For colored flames produced by the rare elements, see Appendix.

(B) PRELIMINARY TESTS FOR ACIDS.

Important conclusions regarding the presence or absence of certain acids may be drawn from the behavior of their salts with dilute and concentrated sulphuric acid, and also with alcohol and sulphuric acid.

1. If a portion of the substance or solution be placed in a test-tube and *dilute sulphuric acid* poured over it, there may be evolved:

Colored Gases: Greenish-yellow chlorine in presence of hypochlorites (see 1, page 83). Moistened potassium iodide starch paper held in the fumes is colored blue.

Red vapors of nitrogen dioxide from nitrites (see 1, page 82).

Colorless Gases recognized by their Odor: Sulphurous anhydride, from sulphites or hyposulphites; in the presence of the latter, separation of sulphur also takes place (see 2, page 63). Detection of sulphurous anhydride by potassium iodate (see 2, page 61).

Hydrocyanic acid, from many of the cyanides, recognized by its odor of bitter almonds, and also by the sulphocyanide reaction (see 5, page 78).

Acetic acid in presence of acetates.

Hydrogen sulphide, from many of the sulphides, blackens paper saturated with solution of plumbic acetate (see 4, page 81). Polysulphides evolve hydrogen sulphide, with the separation of sulphur; sulpho-acids may also separate. (See pages 121, 122.)

Colorless and Odorless Gas: Carbon dioxide is liberated with effervescence from carbonates (to be confirmed with calcium hydroxide, see 2, page 68).

2. If a small portion of the substance is treated with three or four times its volume of *concentrated sulphuric acid* and gently warmed, there may be evolved:

Colored Gases: Greenish-yellow chlorine in presence of hypochlorites; also when both chlorides and nitrates, or chlorides and peroxides are present. (When chlorides and nitrates are present, hydrochloric acid and nitric acid are simultaneously liberated and react upon each other (see *d*, page 106). When chlorides and peroxides are present, the liberated hydrochloric acid acts upon the peroxides (see *c*, page 106).)

Greenish-yellow explosive mixture of chlorine and chlorine tetroxide, derived from chlorates (see 4, page 86).

Brownish bromine together with hydrobromic acid derived from bromides; the gas colors starch paper reddish yellow.

Brownish-red chromium oxychloride when chlorides and chromates are both present (see 4, page 74).

Reddish-brown fumes indicate nitrites (see 1, page 82).

Violet vapors of iodine from iodides color moistened starch paper blue.

Colorless Gases recognized by their Odor: Hydrochloric acid

vapors from chlorides; pungent odor, and render argentic nitrate solution (on glass rod) turbid (see 2, page 73).

Hydrobromic acid (see above).

Hydrofluoric acid from fluorides; of a strongly acid odor, etches glass (see 4, page 67).

Nitric acid from nitrates, pungent odor. Red vapors arise when ferrous sulphate is added.

Sulphurous anhydride from sulphites and hyposulphites (see 2, page 61, and 2, page 63.—N.B. May also result from the reduction of the sulphuric acid employed).

Hydrogen sulphide from sulphides (see 4, page 81).

Acetic acid from acetates, odor of vinegar (see 5, page 87).

Colorless and Odorless Gases: Oxygen (recognized by test with glowing wood, see 7, page 93) in presence of peroxides, chromates, and permanganates; for example:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O;$$

$$2K_2CrO_4 + 5H_2SO_4 = Cr_2(SO_4)_3 + 2K_2SO_4 + 5H_2O + O_3;$$

$$2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + O_5.$$

Chromates become green in color; permanganates are decolorized.

Carbon dioxide from carbonates, effervescence (see 2, page 68).

Carbon monoxide (burns with bluish flame) from organic substances, usually with blackening of the substance and the evolution of carbon dioxide and sulphurous anhydride, as in the case of tartaric acid. Carbon monoxide together with carbon dioxide is evolved from oxalic acid (without blackening, see 6, page 88). From cyanides, ferrocyanides, etc. (Cyanides, page 110).

In presence of the latter a transitory bluish coloration appears.

3. If a portion of the substance is heated with *concentrated sulphuric acid and alcohol,* there is produced, in the presence of acetates, ethyl acetate, which may be recognized by its apple-like odor (see 6, page 87). If the alcohol is ignited, the flame assumes a green color in presence of boric acid (see 5, page 66).

IV. SOLUTION AND FUSION.

Solids must necessarily be in *solution* in order to make the tests in the Wet Way. The method employed in dissolving the solid depends upon the nature of the substance; with this in view, substances may be divided into the following five groups:

1. Oxides and salts (in general).
2. Metals and alloys.
3. Sulphides (of the heavy metals).
4. Cyanides (of the heavy metals).
5. Silicates.

A distinction may be made between solution and fusion. Many salts cannot be directly dissolved in water or acids, but must undergo a special treatment to separate the acids from the bases, as in the case of barium sulphate; the sulphuric acid is separated from the barium by fusing with sodium carbonate. By fusion, new compounds of the bases and acids are obtained which are soluble in water or acids.

In case a substance is not entirely soluble in any one of the solvents, it should be treated by each solvent in turn, and the solutions analyzed separately, as two simple analyses are more quickly made than one complex one. For example, the substance is first boiled with water, the solution obtained is filtered off and set aside for examination, any residue insoluble in hot water is treated with nitric acid and the solution examined separately, any residue remaining after treatment with nitric acid is treated with hydrochloric acid. By this pro-

cedure a more distinct insight into the nature of the substance to be analyzed is obtained.

Hard bodies, minerals, etc., must be pulverized in a porcelain or agate mortar before they are dissolved. Very hard minerals are first crushed in a steel mortar, and the coarse powder thus obtained is afterwards pulverized in an agate mortar. It is advisable to sift the powder through a linen cloth (previously washed and dried), remove the coarser particles and again pulverize them, and repeat the operation.

If the substance to be analyzed be an organic compound or contain organic material (as shown by the preliminary examination), the organic substance must be destroyed by ignition and the residue then dissolved in water (removing by filtration any separated carbon).

1. DISSOLVING OXIDES AND SALTS.

(*a*) A portion of the substance to be dissolved is heated in a test-tube, with water. In case it enters into solution, a larger portion is dissolved and the liquid employed in testing for bases and acids. If the substance is apparently undissolved, it is separated by filtration and the filtrate evaporated to dryness, to ascertain whether any of the original substance entered into solution.

(*b*) Substances insoluble in water are further tested as to their solubility in dilute nitric acid. An excess of nitric acid should be avoided, as many nitrates soluble in water are insoluble in excess of strong acids.

On dissolving oxides with nitric acid, nitrates are formed, and on dissolving salts, nitrates of the bases are produced with the liberation of the acids which were in combination; for example:

$$Ca_3(PO_4)_2 + 6HNO_3 = 3Ca(NO_3)_2 + 2H_3PO_4;$$
$$CuCO_3 + 2HNO_3 = Cu(NO_3)_2 + CO_2 + H_2O.$$

Thus the presence of volatile acids becomes evident:

Carbonic acid: effervesces; odorless gas; renders calcium hydroxide solution turbid (see 2, page 68).

Hydrocyanic acid: odor of bitter almonds; forms ammonium sulphocyanide with ammonium sulphide (see 5, page 78).

Hydrogen sulphide: recognizable by its odor; blackens paper saturated with solution of plumbic acetate (see 4, page 81).

Sulphurous acid: odor of burning sulphur; colors potassium iodate starch paper blue (see 2, page 61).

Under certain conditions the presence of iodine, bromine, or chlorine may become evident (see 2, page 100).

In using nitric acid as a solvent, acids which are soluble with difficulty may separate: Boric acid, crystalline, easily soluble in hot water; silicic acid, gelatinous.

Reddish-brown fumes of nitrogen dioxide result from the processes of oxidation; for example, when mercurous compounds are converted into mercuric compounds:

$$Hg_2O + 6HNO_3 = 2Hg(NO_3)_2 + 2NO_2 + 3H_2O.$$

These oxidations may interfere with the results of the analysis, especially when compounds of mercury are present. After the oxidation with nitric acid it is impossible to determine the original condition of oxidation of the salt; for example, in the case of mercury, after oxidation it cannot be ascertained whether the salt was present originally as a mercurous or a mercuric salt. Salts of mercury which are insoluble in water or in moderately warm dilute nitric acid are decomposed by boiling in sodium hydroxide (compare page 106, *e*). Compounds of arsenic should be dissolved, when possible, in hydrochloric acid, in order to prevent the conversion of arsenious acid into arsenic acid. Plumboso-plumbic oxide (red lead) when treated with dilute nitric acid is decom-

posed into soluble plumbic nitrate and insoluble, brown lead dioxide:

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

The latter is converted into plumbic chloride by concentrated hydrochloric acid.

(*c*) Those substances which are insoluble in dilute nitric acid must be treated with concentrated hydrochloric acid. If in dissolving the substance in hydrochloric acid chlorine gas is evolved, peroxides and similar compounds, such as manganese dioxide, chromic acid, or permanganic acid, are present:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O;$$
$$2CrO_3 + 12HCl = Cr_2Cl_6 + Cl_6 + 6H_2O;$$
$$Mn_2O_7 + 14HCl = 2MnCl_2 + Cl_{10} + 7H_2O.$$

Lead dioxide is converted into plumbic chloride, which crystallizes as the solution cools; it is best decomposed with sodium carbonate (page 106, *e*).

(*d*) Many compounds insoluble in nitric acid or in hydrochloric acid are soluble in nitro-hydrochloric acid (aqua regia).

In dissolving with nitro-hydrochloric acid chlorine[1] is liberated, which is the active agent in effecting solution:

$$3HCl + HNO_3 = Cl_3 + NO + 2H_2O.$$

Nitro-hydrochloric acid is prepared by mixing about three volumes of concentrated hydrochloric acid with one volume of concentrated nitric acid; the reaction takes place upon the application of heat. When nitro-hydrochloric acid is employed as a solvent, oxidation necessarily occurs if the substance is capable of being oxidized, as, for example, with compounds of mercury.

(*e*) Many compounds that are insoluble in water and in acids are decomposed by boiling or fusing with carbonates of the alkalies,—that is, they are converted into soluble com-

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[1] Besides (NOCl) nitrosyl chloride and (NO_2Cl) nitroxyl chloride.

pounds. Among them are plumbic sulphate, the sulphates of the alkaline earths, plumbic chloride, plumbic iodide, stannic oxide, etc.

Of the sulphates, plumbic sulphate and calcium sulphate are easily decomposed by boiling in a solution of sodium carbonate. Precipitated strontium sulphate is also decomposed in the same manner, although with more difficulty. Precipitated barium sulphate is only partly decomposed by boiling with sodium carbonate solution. These sulphates (as well as minerals) are readily decomposed by being fused with from four to six parts of sodium potassium carbonate.[1] In these decompositions the acid of the substance fused unites with the alkalies, and the base is converted into a carbonate; for example, with $BaSO_4$ and $NaKCO_3$ the compounds $NaKSO_4$, soluble in water, and $BaCO_3$, soluble in acids, are formed:

$$NaKCO_3 + BaSO_4 = NaKSO_4 + BaCO_3.$$

The fused mass is completely extracted with hot water and the insoluble residue (after separation by filtering) is dissolved in hydrochloric acid or nitric acid. The aqueous solution is to be examined for the acid, and the acid solution for the base.

Plumbic chloride and plumbic iodide, etc., when boiled with a solution of sodium carbonate, are decomposed respectively into chloride and iodide of sodium and plumbic carbonate:

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[1] The double salt $NaKCO_3$ fuses more easily than the sodium or potassium salt alone. The fusion is best made in a platinum crucible, as porcelain is attacked by the alkali carbonates. The following substances should never be fused in a platinum crucible: potassium and sodium hydroxide, nitrates and cyanides of the alkalies, metals and metallic sulphides, or any substance from which a metal may be obtained by reduction or substances from which chlorine may be evolved.

$$PbCl_2 + Na_2CO_3 = 2NaCl + PbCO_3.$$

(Plumbic carbonate is slightly soluble in sodium carbonate.)

Stannic oxide (cassiterite) when fused with a carbonate of an alkali is converted into a stannate of the alkali, which is soluble in water and in hydrochloric acid:

$$SnO_2 + K_2CO_3 = SnO(OK)_2 + CO_2;$$

$$SnO(OK)_2 + 6HCl = SnCl_4 + 2KCl + 3H_2O.$$

Fusion is continued until carbon dioxide ceases to be evolved. As stannic oxide is acted upon only with great difficulty by sodium carbonate, it is best fused in a silver crucible with sodium or potassium hydroxide,[1] and the fused mass treated with water and hydrochloric acid, as mentioned above.

Many substances are unacted upon by the carbonates of the alkalies, but are readily decomposed on being boiled with sodium or potassium hydroxide; for example, mercury and silver compounds. An oxide of the metal is formed, while the acid remains in solution in combination with the alkali. The oxide after being washed is dissolved in nitric acid.

$$Hg_2Cl_2 + 2NaOH = Hg_2O + 2NaCl + H_2O.$$

In dissolving compounds of mercury cold dilute nitric acid should be used, in order to avoid the oxidation of mercurous salts to mercuric salts. (Mercuric iodide, which partly redissolves in a carbonate of an alkali,—*i.e.*, in the iodide of the alkali which is formed,—should be dissolved in nitro-hydrochloric acid.)

(*f*) Compounds of fluorine (for example, fluor spar) are decomposed by being gently heated with concentrated sulphuric acid in a platinum crucible:

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[1] Or it may be fused in a porcelain crucible with three parts of sodium carbonate and three parts of sulphur to one part of the substance, and the fused mass, after cooling, extracted with water. The yellow solution contains the tin as sulphostannate, Na_2SnS_3; the insoluble residue, containing sulphides, is to be examined further according to 3, page 111.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The hydrofluoric acid is recognized by its etching glass (see 4, page 67); the residue in the crucible, consisting of sulphates, is dissolved in hydrochloric acid or, if necessary, fused with sodium carbonate.

Silicates containing fluorine, if treated in this manner, yield silicon fluoride, according to the reaction:

$$2CaF_2 + SiO_2 + 2H_2SO_4 = SiF_4 + 2CaSO_4 + 2H_2O.$$

If the evolved gas be conducted through a glass tube moistened with water, silicic acid together with hydrofluosilicic acid is produced:

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3.$$

The silicic acid will appear, either directly or on drying the tube, in the form of a white coating (see 5, page 68).

(*g*) Chromic oxide, chromite, aluminium oxide, and ferric oxide are best fused by mixing them with ten parts of acid potassium sulphate. If the heat applied is not too great, neutral sulphates (together with basic salts) are formed:

$$Al_2O_3 + 6KHSO_4 = Al_2(SO_4)_3 + 3K_2SO_4 + 3H_2O,$$

which, on cooling, may be dissolved by water or hydrochloric acid.

Chromite is best fused with acid potassium sulphate, and the fused mass obtained again fused with potassium chlorate and potassium carbonate, to convert the chromic oxide into chromic acid:

$$Cr_2(SO_4)_3 + 3K_2CO_3 = Cr_2O_3 + 3K_2SO_4 + 3CO_2;$$

$$Cr_2O_3 + 2K_2CO_3 + KClO_3 = 2K_2CrO_4 + KCl + 2CO_2.$$

The fused mass yields potassium chromate when extracted with water; the residue, consisting of ferric oxide (with some chromic oxide) is dissolved in hydrochloric acid.

(*h*) Carbon (charcoal, graphite) and sulphur are recognized by their appearance and their behavior when heated.

2. THE DISSOLVING OF METALS AND ALLOYS.

Metals and alloys are treated with concentrated nitric acid and heated until red vapors cease to be produced upon the further addition of acid. The excess of nitric acid (which would interfere with the solubility of the nitrates in water) is evaporated on the water-bath, and the residue dissolved with water and a little nitric acid. Most of the metals enter into solution as nitrates, gold, platinum, etc., remain unchanged, and tin and antimony remain as oxides or hydroxides.[1]

In the presence of tin or antimony arsenic may be found in the residue, in the arsenic condition. The residue, after thorough washing, is digested with yellow ammonium sulphide, whereby tin, antimony, and arsenic enter into solution as sulpho-salts:

$$Sn(OH)_4 + 3(NH_4)_2S = (NH_4)_2SnS_3 + 4NH_3 + 4H_2O;$$
$$Sb_2O_3 + 6(NH_4)_2S + S_2 = 2(NH_4)_3SbS_4 + 6NH_3 + 3H_2O;$$
$$Sb_2O_4 + 7(NH_4)_2S + S = 2(NH_4)_3SbS_4 + 8NH_3 + 4H_2O;$$
$$Sb_2O_5 + 8(NH_4)_2S = 2(NH_4)_3SbS_4 + 10NH_3 + 5H_2O;$$
$$As_2O_5 + 8(NH_4)_2S = 2(NH_4)_3AsS_4 + 10NH_3 + 5H_2O.$$

If an insoluble residue remain, it is again treated with nitric acid; if it still fail to dissolve, it is finally treated with nitro-hydrochloric acid, which dissolves gold and platinum as chlorides:

$$Au + 3HCl + HNO_3 = AuCl_3 + NO + 2H_2O;$$
$$3Pt + 12HCl + 4HNO_3 = 3PtCl_4 + 4NO + 8H_2O.$$

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[1] In dissolving metals in nitric acid different oxides of nitrogen are produced, depending upon the concentration of the acid employed. With nitric acid of 1.42 specific gravity NO_2 is produced; with an acid of 1.35 specific gravity, principally N_2O_3; with an acid of 1.2 specific gravity NO; and with an acid of 1.1 specific gravity N_2O. (With an acid of greater dilution ammonia is produced.) Nitric acid of 1.1 or less specific gravity is decomposed only by the more strongly positive metals; for example, Zn and Fe.

3. SULPHIDES OF THE HEAVY METALS.

The sulphides of the heavy metals generally possess a metallic lustre; like the metals they are treated with concentrated nitric acid, whereby most of them are dissolved as nitrates:

$$CuS + 4HNO_3 = Cu(NO_3)_2 + S + 2NO_2 + 2H_2O.$$

The procedure is as given under 2, page 110. The sulphur which separates first is oxidized by the nitric acid to sulphuric acid. The insoluble residue, in addition to the oxides of tin, antimony, and arsenic, may contain $PbSO_4$, $BiONO_3$ (formed on treating the nitrate with water), and HgS. This residue is treated with yellow ammonium sulphide, which dissolves tin, antimony, and arsenic. Any residue remaining is filtered off and treated with nitric acid to dissolve the lead and bismuth (which at this stage may be found again as sulphides), and any residue of mercuric sulphide is collected on a filter and dissolved by nitro-hydrochloric acid:

$$3HgS + 6HCl + 2HNO_3 = 3HgCl_2 + 2NO + 4H_2O + S_3.$$

Finally silicious gangue, barite, etc., may remain, which should be examined according to 5 (page 113) and 1 (page 104) respectively.

The sulphides are easily recognized by their appearance, and also by their behavior in the preliminary examination.

4. CYANIDES.

The simple cyanides, which are insoluble in water, may be decomposed into chlorides and hydrocyanic acid, by boiling with concentrated hydrochloric acid.

Argentic cyanide and mercuric cyanide, in which the cyanogen cannot be detected by the ordinary methods, may be readily recognized by their behavior when heated, as they separate into metal and cyanogen. If the cyanide is heated

in a narrow glass tube, the escaping cyanogen may be ignited, burning with a pinkish-lavender flame. The gas is also recognizable by its odor of bitter almonds. Mercuric cyanide may be decomposed by dissolving in water and passing hydrogen sulphide through the solution; mercuric sulphide is precipitated and hydrocyanic acid enters into solution.

The insoluble compounds of ferrocyanogen and ferricyanogen are decomposed by boiling with sodium carbonate or sodium hydroxide; sodium ferrocyanide and ferricyanide respectively are formed, together with an insoluble carbonate or an oxide of the metal:

$$Pb_2Fe(CN)_6 + 2Na_2CO_3 = Na_4Fe(CN)_6 + 2PbCO_3;$$
$$Cu_2Fe(CN)_6 + 4NaOH = Na_4Fe(CN)_6 + 2CuO + 2H_2O.$$

The aqueous solution is filtered and the filtrate tested for the acid, while the carbonates or oxides are dissolved in dilute nitric acid. If sodium hydroxide is employed as the decomposing agent, lead, zinc, and aluminium, and also arsenic, antimony, and tin, may enter into solution. In such cases a portion of the alkaline solution is tested for lead, zinc, and aluminium by saturating the solution with hydrogen sulphide, thereby precipitating the first two metals as sulphides and the last as hydroxide. The filtrate from any precipitate which may have been produced, or the clear solution if no precipitate was produced by hydrogen sulphide, is acidulated with hydrochloric acid to precipitate arsenic, antimony, and tin as sulphides.

If sodium hydroxide is used in decomposing the ferricyanide, sodium ferricyanide is formed, providing the metallic oxide produced in the operation is not further oxidizable:

$$Cu_3(Fe(CN)_6)_2 + 6NaOH = 2Na_3Fe(CN)_6 + 3CuO + 3H_2O.$$

If, however, the separated oxide is capable of further oxidation, this oxidation takes place, accompanied by the reduction of the sodium ferricyanide to sodium ferrocyanide:

$$Fe_3(Fe(CN)_6)_2 + 8NaOH = 2Na_3Fe(CN)_6 + 3Fe(OH)_2 + 2NaOH;$$

$$2Na_3Fe(CN)_6 + 3Fe(OH)_2 + 2NaOH = 2Na_4Fe(CN)_6 + Fe_2(OH)_6 + Fe(OH)_2.$$

Consequently, in such cases to detect the acid the substance is fused, whenever possible, with sodium carbonate.

To detect alkalies in ferrocyanogen and ferricyanogen compounds, the latter are decomposed into sulphates, carbon monoxide, and ammonium sulphate, by being heated with concentrated sulphuric acid:

$$CuK_2Fe(CN)_6 + 6H_2SO_4 + 6H_2O = FeSO_4 + CuSO_4 + K_2SO_4 + 6CO + 3(NH_4)_2SO_4.$$

5. SILICATES.

Before silicates can be analyzed they must be finely pulverized (page 104).

(*a*) Silicates soluble in water or silicates that may be decomposed by acids are best decomposed by being boiled with concentrated hydrochloric acid; by this procedure silicic acid and chlorides of the respective metals are formed; for example:

$$K_2SiO_3 + 2HCl = H_2SiO_3 + 2KCl.$$

Boiling is continued until complete decomposition has taken place, and no gritty particles are detected on stirring with a glass rod. The solution is then evaporated to the dryness of dust on a water-bath (see 1, page 69), to convert the soluble silicic acid into insoluble amorphous silicic acid. The dry residue is then moistened with a little concentrated hydrochloric acid, to convert any basic chlorides (of Fe, Al, Mg, etc.) into neutral chlorides, thereby rendering them soluble; finally the chlorides of the bases are extracted with water and dilute hydrochloric acid.

(*b*) Silicates that are not decomposed by acids must either be fused with a carbonate of an alkali or decomposed by

hydrofluoric acid. To determine which method should be employed, the silicate is tested for the presence of an alkali. For this purpose a small portion of the powdered silicate, moistened with hydrochloric acid, is placed on a platinum wire and held in the non-luminous flame of a Bunsen burner, to observe whether a color is imparted to the flame (sodium, yellow; potassium, violet). If alkalies are absent the method of decomposition by means of sodium carbonate is to be employed; whereas if alkalies are present, in order to test for them, the silicate must be decomposed with hydrofluoric acid.

(*c*) In case the fusion is to be made with sodium carbonate (preferably with sodium potassium carbonate), one part of the finely pulverized substance is thoroughly mixed with six parts of sodium potassium carbonate, placed in a platinum crucible, and the mixture fused by means of the blast-lamp. The silicate is decomposed by the carbonate of an alkali, with the production of a silicate of the alkali (or at least silicates that are decomposed by acids) and a carbonate of the metal:

$$CaSiO_3 + NaKCO_3 = NaKSiO_3 + CaCO_3;$$

$$CaSi_2O_5 + 2NaKCO_3 = 2NaKSiO_3 + CaCO_3 + CO_2.$$

On disintegrating the fused mass with hydrochloric acid, according to *a*, page 113, silicic acid remains insoluble, and the chlorides of the metals together with sodium chloride and potassium chloride enter into solution.

(*d*) In using hydrofluoric acid as a solvent the finely pulverized substance is placed in a platinum crucible, and treated with the pure acid[1] until a thin paste is formed. The mixture is stirred with a platinum wire (not with a glass rod) and digested, at a very gentle heat, until the substance is completely dissolved. By this treatment the silicates are converted into fluosilicates:

---

[1] The hydrofluoric acid must be free from alkalies, and, when possible, freshly distilled in a platinum still.

$$CaSiO_3 + 6HF = CaSiF_6 + 3H_2O;$$

$$CaSi_2O_5 + 12HF = CaSiF_6 + H_2SiF_6 + 5H_2O.$$

When completely dissolved concentrated sulphuric acid is added and heat applied, gently at first, but afterwards more strongly, to drive off the excess of acid. The sulphuric acid converts the fluosilicates into sulphates, while hydrofluosilicic acid is evolved:

$$CaSiF_6 + H_2SO_4 = H_2SiF_6 + CaSO_4.$$

The residue of sulphates is dissolved in water and a little hydrochloric acid.

When this method is employed to decompose silicates containing barium, strontium, or calcium, it is necessary—especially with barium and strontium,—to afterwards fuse the residue containing the barium, strontium, or calcium sulphate with a carbonate of an alkali (page 106).

In mineral analyses it is often of interest to ascertain whether the minerals contain, in addition to the silicates not decomposable by acids, others that may be decomposed, thus making separation possible. With this in view, after having mechanically separated the gangue and any other impurities from the mineral proper, it is finely pulverized, treated with hydrochloric acid, the solution evaporated to dryness as above described (page 113, *a*), and the chlorides resulting from the decomposed silicates dissolved in water. The insoluble residue, which may contain silicic acid and undecomposed silicates, is boiled with sodium carbonate, which dissolves the silicic acid derived from the decomposed silicate. After acidulating the sodium carbonate solution with hydrochloric acid, evaporating to dryness, and extracting with hot water, the silicic acid remains as a light, white powder. If a residue remain after boiling a second time with sodium carbonate, it is to be considered an undecomposable silicate, which is to be further tested according to *b*, *c*, and *d*, page 114.

V. DETECTION OF BASES IN THE WET WAY.

IF the substance to be analyzed is a solid it is to be dissolved, as before described (page 104).

To test for bases in organic substances the latter should be incinerated and the bases extracted from the ash by water or acids. Organic acids, etc., interfere with a number of the reactions used in the detection of bases.

The reaction of solutions to be examined should be tested with litmus and turmeric paper to ascertain whether they are neutral, acid, or alkaline. A number of substances may be present in acid solutions, which, in neutral solutions, may be disregarded; for example, in the third group, acid solutions must be tested for phosphates and oxalates, whereas if the solutions are neutral the tests for these acids need not be made.

Regarding combinations that may arise during the examination of alkaline solutions see *b*, page 120.

PRECIPITATION OF THE DIFFERENT GROUPS.

To separate the bases into groups the following group reagents are employed:

1. Hydrochloric acid.
2. Hydrogen sulphide.
3. Ammonium hydroxide.
4. Ammonium sulphide.
5. Ammonium carbonate.

By each of these reagents a series of bases called a group is precipitated. Bases that are not precipitated by group reagents are classed as a sixth group. (Table I., pages 118 and 119.) The rare elements are not considered in this plan.

TABLE I.—GROUP PRECIPITATIONS.

GROUP I. Metals precipitated by Hydrochloric Acid.	GROUP II. Metals precipitated by Hydrogen Sulphide.	GROUP III. Metals precipitated by Ammonium Hydroxide.
Silver, as white, curdy $AgCl$, argentic chloride.	*Lead,* as black PbS, plumbic sulphide.	*Iron,* as reddish-brown $Fe_2(OH)_6$, ferric hydroxide.
Mercurous salts, as white, pulverulent Hg_2Cl_2, mercurous chloride.	*Mercuric salts,* as black HgS, mercuric sulphide.	*Chromium,* as dirty-green $Cr_2(OH)_6$, chromic hydroxide.
Lead, as white $PbCl_2$, plumbic chloride.	*Copper,* as black CuS, cupric sulphide.	*Aluminium,* as white, gelatinous $Al_2(OH)_6$, aluminium hydroxide.
	Bismuth, as brownish-black Bi_2S_3, bismuthous sulphide.	In presence of phosphoric acid iron and aluminium respectively are precipitated as phosphates,—thus:
	Stannous salts, as brownish-black SnS, stannous sulphide.	*Iron,* as white $Fe_2(PO_4)_2$, ferric phosphate.
	Cadmium, as yellow CdS, cadmium sulphide.	*Aluminium,* as white $Al_2(PO_4)_2$, aluminium phosphate.
	Arsenic, as yellow As_2S_3, arsenious sulphide (mixed with sulphur if precipitated from arsenic acid solutions).	In presence of phosphoric acid or oxalic acid calcium, strontium, and barium are precipitated as phosphates or oxalates, as white $Ca_3(PO_4)_2$, SrC_2O_4, etc.
	Stannic salts, as yellow SnS_2, stannic sulphide.	Magnesium in the presence of phosphoric acid is precipitated in this group as white $MgNH_4PO_4$, ammonium magnesium phosphate.
	Antimonious salts, as orange-red Sb_2S_3, antimonious sulphide.	In presence of iron, manganese may be precipitated as white, changing to brown, $Mn(OH)_2$, manganous hydroxide.
	Antimonic salts, as orange-red Sb_2S_5, antimonic sulphide (together with Sb_2S_3 and sulphur).	
	Gold, as black Au_2S_3, auric sulphide.	
	Platinum, as brownish-black PtS_2, platinic sulphide.	

TABLE I.—GROUP PRECIPITATIONS.—*Continued.*

GROUP IV. Metals precipitated by Ammonium Sulphide.	GROUP V. Metals precipitated by Ammonium Carbonate.	GROUP VI. For which there is no Special Group Reagent.
Manganese, as light-salmon-colored MnS, manganous sulphide.	*Barium,* as white $BaCO_3$, barium carbonate.	*Magnesium.*
Zinc, as white ZnS, zinc sulphide.	*Strontium,* as white $SrCO_3$, strontium carbonate.	*Potassium.*
Nickel, as black NiS, nickelous sulphide.	*Calcium,* as white $CaCO_3$, calcium carbonate.	*Sodium.*
Cobalt, as black CoS, cobaltous sulphide.		*Lithium.*
		Ammonium.

If on the addition of the reagent a precipitate is formed, it is filtered off and carefully washed. The filtrate should be tested to ascertain whether the precipitation was complete,—that is, whether no precipitation takes place on further addition of the reagent. The precipitate must be collected only on properly-cut filters which fit closely to the inner surface of the funnel, and the liquid in which the precipitate is suspended should be poured into the filter down a glass rod. The precipitates should be thoroughly washed before proceeding with the examination. This is not only good preliminary practice for quantitative work, but is absolutely necessary to obtain exact results in qualitative analysis.

Concentrated solutions should be diluted with water before the examination is commenced. This dilution may cause turbidity, in consequence of the formation of basic salts or oxychlorides of bismuth, antimony, or mercury. These, however, may be redissolved by the addition of a little nitric or hydrochloric acid.

FIRST GROUP.

(*a*) Neutral or acid solutions are treated with a few drops of dilute hydrochloric acid.

There will be precipitated :

Silver, as white, curdy $AgCl$, argentic chloride.

Mercurous salts, as white, pulverulent Hg_2Cl_2, mercurous chloride.

Lead, as white, crystalline $PbCl_2$, plumbic chloride.

The latter is incompletely precipitated, as it is slightly soluble in water ; therefore a test for it must also be made in the second group. The solution in which the precipitation takes place must be cold, as plumbic chloride is easily soluble in hot water and might remain in solution ; moreover, small quantities of mercurous salts might be overlooked in the

presence of nitric acid, as, when hydrochloric acid and nitric acid are both present and the solution is warm, mercurous chloride is transformed into soluble mercuric chloride.

Furthermore, it should be observed whether the precipitate redissolves on the addition of an excess of the hydrochloric acid. On the addition of dilute hydrochloric acid, dilute solutions of compounds of bismuth yield a white precipitate of $BiOCl$, bismuth oxychloride, which on the further addition of hydrochloric acid is redissolved as $BiCl_3$, bismuthous chloride. Compounds of antimony, especially $K(SbO)C_4H_4O_6$, potassium antimonious tartrate, with dilute hydrochloric acid form $SbOCl$, antimonious oxychloride, which is soluble in an excess of the acid as $SbCl_3$, antimonious chloride. $KHC_4H_4O_6$, acid potassium tartrate, if it should have separated, would be redissolved on the further addition of hydrochloric acid:

$$KHC_4H_4O_6 + HCl = H_2C_4H_4O_6 + KCl.$$

Furthermore, there may be precipitated in the first group: boric acid (crystalline), organic acids, and sulphur. (Sulphur separates from hyposulphites and polysulphides:

$$Na_2S_2O_3 + 2HCl = 2NaCl + S + SO_2 + H_2O;$$
$$(NH_4)_2S_3 + 2HCl = 2NH_4Cl + S_2 + H_2S.$$

In the first case sulphurous anhydride, in the latter case hydrogen sulphide, is evolved with the sulphur. Polysulphides are always alkaline in reaction.)

Attention should be paid to any gases evolved on treatment with hydrochloric acid (with reference to the manner of distinguishing them see pages 99 to 102 and 105). Sulphurous anhydride must be driven off by heating; otherwise, on the addition of hydrogen sulphide, separation of sulphur would occur (together with the formation of pentathionic acid):

$$5SO_2 + 5H_2S = H_2S_5O_6 + S_5 + 4H_2O.$$

Chlorine, nitrogen dioxide, etc., should also be expelled by heating the liquid.

(*b*) Alkaline solutions should be treated with hydrochloric acid until acid in reaction, and any formation of precipitates or evolution of gases observed. From alkaline solutions there may be separated:

1. Sulphur and sulphides of the metals, accompanied by the evolution of hydrogen sulphide.

The sulphides are the following sulpho-acids: As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS_2: they should be tested according to the directions given in the chapter treating of them under the second group (see B, page 135). Under certain conditions CuS, HgS, and NiS might also be encountered at this stage. The filtrate from the sulphur or the sulphides which have separated may be examined directly for the metals of the fifth and sixth groups.

2. Cyanides of the heavy metals (which were dissolved in cyanides of the alkalies), with the evolution of hydrocyanic acid. Concentrated hydrochloric acid is added to the liquid containing the precipitate and the whole heated. The cyanides are thereby converted into chlorides, which finally dissolve, argentic chloride alone remaining undissolved. The solution is then examined for the presence of metals of the second, third, and subsequent groups; argentic chloride in the residue is confirmed by testing its solubility in ammonium hydroxide.

3. Silicic acid: gelatinous; should be confirmed in the bead of microcosmic salt (see 4, page 70). The solution, together with the precipitate, is treated with an excess of hydrochloric acid, and evaporated to dryness on the water-bath to render the silicic acid insoluble. The residue is extracted with water and a little hydrochloric acid (page 113, *a*), and the filtrate examined for bases. It usually contains nothing but the alkalies.

4. Precipitates of plumbic hydroxide, aluminium hydroxide, chromium hydroxide, and zinc hydroxide may be formed, but on acidifying with hydrochloric acid will immediately disappear, being converted into soluble chlorides.

SECOND GROUP.

Hydrogen sulphide is conducted into the acid filtrate obtained from the precipitate of the first group, or into the solution in which hydrochloric acid failed to produce a precipitate, until a distinct odor of the gas is observable in the liquid.

There will be precipitated:

Lead, as black PbS, plumbic sulphide.
Mercuric salts, as black HgS, mercuric sulphide.
Copper, as black CuS, cupric sulphide.
Bismuth, as brownish-black Bi_2S_3, bismuthous sulphide.
Gold, as black Au_2S_3, auric sulphide.
Platinum, as brownish-black PtS_2, platinic sulphide.
Cadmium, as yellow CdS, cadmium sulphide.
Arsenious compounds, as yellow As_2S_3, arsenious sulphide.
Arsenic compounds, as yellow As_2S_3, arsenious sulphide (with sulphur).
Antimonious compounds, as orange-red Sb_2S_3, antimonious sulphide.
Antimonic compounds, as orange-red Sb_2S_5, antimonic sulphide (together with Sb_2S_3 and S).
Stannous compounds, as brownish-black SnS, stannous sulphide.
Stannic compounds, as yellow SnS_2, stannic sulphide.

From solutions containing hydrochloric acid, when hydrogen sulphide is not present in sufficient quantity, lead is precipitated as red Pb_2SCl_2, plumbic sulphochloride, which is

converted by further addition of hydrogen sulphide into black PbS. In solutions of mercuric salts white precipitates of double salts (for example, $Hg_3S_3Cl_2$) are formed, which on continuing the addition of hydrogen sulphide become yellow, then brown, and finally are converted into black HgS. Arsenious acid is precipitated at once, arsenic acid gradually; the precipitation is accelerated, however, by heating (see 1, page 26).

Sulphur may also separate when hydrogen sulphide is introduced into the solution. This separation may be caused by:

1. Chlorine, bromine, iodine, nitrous acid, nitrogen dioxide, etc. (in consequence of their oxidizing action upon hydrogen sulphide); for example:

$$Cl_2 + H_2S = 2HCl + S;$$

$$N_2O_3 + H_2S = 2NO + H_2O + S.$$

On passing hydrogen sulphide into solutions containing an excess of nitric acid or nitro-hydrochloric acid, sulphur is separated. The excess of acid should be driven off by evaporation and, after diluting with water, the introduction of hydrogen sulphide should be repeated.

2. Sulphurous acid (page 121).

3. Ferric salts, in consequence of their reduction to ferrous salts:

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

Decolorization of the solution results from the reduction.

4. Chromic acid and chromates, in consequence of their reduction to chromic salts:

$$2H_2CrO_4 + 3H_2S + 6HCl = Cr_2Cl_6 + 8H_2O + S_3.$$

The solution changes in color from yellow to green. By repeated introduction of hydrogen sulphide accompanied by renewed additions of hydrochloric acid, the chromic acid is completely decomposed. If the acid is not added in sufficient

quantity, a precipitate is formed consisting either of green chromic hydroxide:

$$2H_2CrO_4 + 3H_2S = Cr_2(OH)_6 + S_3 + 2H_2O,$$

or of brown chromium chromate:

$$3H_2CrO_4 + 3H_2S = (CrO)_2CrO_4 + S_3 + 6H_2O.$$

5. Permanganic acid and permanganates, in consequence of their reduction to manganous compounds:

$$2HMnO_4 + 5H_2S + 4HCl = 2MnCl_2 + S_5 + 8H_2O.$$

The purplish-red solution is decolorized. The procedure is the same as in 4, page 124. (If the hydrochloric acid is not added in sufficient quantity, brown precipitates are formed.)

THIRD GROUP.

From the filtrate of the second group, or from the solution in which hydrogen sulphide failed to produce a precipitate, the hydrogen sulphide is expelled by boiling. A small quantity of nitric acid is added and the solution warmed to oxidize the bases, ammonium chloride and afterwards ammonium hydroxide (the latter in not too great excess) are added, and the solution is boiled until the odor of ammoniacal gas can no longer be detected.

There will be precipitated:

Iron, as reddish-brown $Fe_2(OH)_6$, ferric hydroxide.
Chromium, as dirty-green $Cr_2(OH)_6$, chromic hydroxide.
Aluminium, as white, gelatinous $Al_2(OH)_6$, aluminium hydroxide.

In the presence of phosphoric or oxalic acids,—

Ferric phosphate, $Fe_2(PO_4)_2$ (white).
Aluminium phosphate, $Al_2(PO_4)_2$ (white).
Phosphates and oxalates of calcium, strontium, barium, $\left\{ \begin{array}{l} Ca_3(PO_4)_2\text{, etc. (white).} \\ CaC_2O_4\text{, etc. (white).} \end{array} \right.$
Ammonium magnesium phosphate, $MgNH_4PO_4$ (white).

In presence of iron some manganese may be precipitated as $Mn(OH)_2$, manganous hydroxide.

The hydrogen sulphide must be expelled, so that, on the addition of the ammonium hydroxide, ammonium sulphide may not form and thereby precipitate the fourth group with the third. By means of the nitric acid ferrous salts are converted into ferric salts; in presence of ammonium chloride the ferrous salts are not precipitated, or are precipitated only incompletely. If the oxidation is not complete, a greenish precipitate is obtained in the presence of ferrous salts, which, when exposed to the air, oxidizes and gradually changes to black and finally to reddish-brown (ferric hydroxide).

In solutions containing silicates the ammonium hydroxide may precipitate gelatinous H_2SiO_3, silicic acid. H_2SO_4 may possibly be formed (by the oxidation of the H_2S passed into the solution), and precipitate barium and strontium as sulphates. Ammonium chloride is added to prevent the precipitation of manganese and magnesium (see 3, page 45, and 1, page 53). The ammonium chloride should be added in excess,—but not too great excess, as thereby the precipitation of the fifth group is unnecessarily rendered more difficult. After the addition of the ammonium hydroxide it is necessary to boil the liquid until the odor of ammonia disappears, in order to completely precipitate aluminium and chromium (see 1, page 41, and 1, page 42). By this procedure the excess of ammoniacal gas is expelled; but the boiling should not be continued too long, as the solution may become acid (in consequence of the decomposition of NH_4Cl with the liberation of NH_3).

FOURTH GROUP.

To the filtrate from the third group (to which ammonium hydroxide is again added), or to the solution in which ammonium chloride and ammonium hydroxide failed to produce a precipitate, colorless or slightly yellow ammonium sulphide is added.

There will be precipitated:

Manganese, as light-salmon-colored MnS, manganous sulphide.

Zinc, as white ZnS, zinc sulphide.

Nickel, as black NiS, nickelous sulphide.

Cobalt, as black CoS, cobaltous sulphide.

Nickelous sulphide is slightly soluble in an excess of yellow ammonium sulphide, imparting a brown color to the solution. The nickelous sulphide is completely separated on boiling the solution, especially after the addition of acetic acid. Ammonium sulphide might also precipitate iron as ferrous sulphide, in case the iron were held in solution by organic substances.

FIFTH GROUP.

From the filtrate of the fourth group, or from the solution in which ammonium sulphide failed to produce a precipitate, the ammonium sulphide is expelled by boiling, any sulphur which may have separated is filtered off, ammonium hydroxide and ammonium carbonate are added to the filtrate, and the whole is boiled as long as carbon dioxide is evolved.

There will be precipitated:

Barium, as white $BaCO_3$, barium carbonate.

Strontium, as white $SrCO_3$, strontium carbonate.

Calcium, as white $CaCO_3$, calcium carbonate.

On the addition of commercial ammonium carbonate, acid carbonates soluble in water—as, for example, $Ca(HCO_3)_2$—

are produced (page 50), which, on boiling, are converted into neutral, insoluble carbonates, with the liberation of CO_2 and H_2O:

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O.$$

The carbonates are soluble in an excess of ammonium chloride on long-continued boiling:

$$CaCO_3 + 2NH_4Cl = CaCl_2 + 2NH_3 + CO_2 + H_2O.$$

SIXTH GROUP.

In this group are classed magnesium, potassium, sodium, and lithium. Ammonium is also classed with this group, but the test for it must be made in the original substance presented for analysis.

(With reference to their separation see Separation of the Sixth Group, page 152.)

With this group may also be found the ferro- and ferricyanides of the alkalies, cobalticyanides of the alkalies, etc., from which the iron and cobalt are not precipitated by the ordinary reagents. Furthermore, aluminium may have remained in solution, because of the presence of organic substances. These compounds are to be treated with concentrated sulphuric acid (page 113) and separated by the regular group precipitations.

SEPARATION OF THE BASES CONTAINED IN THE GROUP PRECIPITATES.

The group precipitates thus obtained are now examined separately. The precipitates of the second and fourth groups must be examined immediately, as they oxidize when exposed to the air. Precipitates of the third group must be quickly

filtered, in order to prevent the formation and precipitation of manganic hydroxide; for example:

$$2MnCl_2(NH_4Cl)_2 + 4NH_4OH + H_2O + O = Mn_2(OH)_6 + 8NH_4Cl.$$

If no precipitate is formed in the third group, ammonium sulphide should be added rapidly, to prevent the separation of manganic hydroxide. If arsenic or tin be found in the second group, a portion of the filtrate is reserved for the tests for acids and the other portion is used in testing for bases.

The filtrate, including the wash-water, from each group precipitation is reserved for treatment with the succeeding group reagent. If no precipitate is produced by a group reagent, it indicates that the metals of that particular group are absent. The solution is then treated with the succeeding group reagent.

SEPARATION OF THE FIRST GROUP.

The precipitate produced by hydrochloric acid, after being washed with cold water, is treated while on the filter with hot water; any plumbic chloride present is dissolved by the hot water, and may be tested for in the filtrate by the addition of sulphuric acid, the formation of a white precipitate of $PbSO_4$ indicating the presence of lead. Argentic chloride and mercurous chloride would remain on the filter, undissolved by the hot water. Any residue remaining on the filter is washed with hot water until free from lead (test washings with H_2SO_4), and then treated with ammonium hydroxide: mercurous chloride is converted into black, insoluble NH_2Hg_2Cl, dimercurous ammonium chloride, while argentic chloride is dissolved as NH_3AgCl, argent-ammonium chloride. The ammoniacal filtrate is treated with nitric acid until acid in reaction. A white precipitate of AgCl indicates the presence of silver.

TABLE II.—SEPARATION OF THE FIRST GROUP.

The precipitate, which may contain $AgCl$, Hg_2Cl_2, $PbCl_2$, is treated, while on the filter, with hot water:

<table>
<tr><td rowspan="2">Filtrate.
$PbCl_2$.
Treat with H_2SO_4:
white precipitate of $PbSO_4$ indicates presence of lead.</td><td colspan="2">Insoluble Residue.
$AgCl$, Hg_2Cl_2.
Treat with ammonium hydroxide:</td></tr>
<tr><td>Filtrate.
Ag
(as NH_3AgCl).
Treat with HNO_3:
white, curdy precipitate of $AgCl$ indicates presence of silver.</td><td>Residue.
Hg
as black
NH_2Hg_2Cl indicates presence of mercurous salts.</td></tr>
</table>

To detect small quantities of argentic chloride in the presence of mercurous chloride, the dry mixture of the chlorides is heated in a small glass tube: mercurous chloride will volatilize, while argentic chloride remains as a horny mass, which may be further tested on charcoal with the blowpipe.

SEPARATION OF THE SECOND GROUP.

Of the sulphides of the second group some are basic and others acid in character; therefore some of them are unacted upon by ammonium sulphide, while others are dissolved as sulpho-salts.

Insoluble.	*Soluble.*
Lead sulphide.	Arsenious sulphide.
Mercuric sulphide.	Antimonious sulphide.
Cupric sulphide.	Antimonic sulphide.
Bismuthous sulphide.	Stannous sulphide.
Cadmium sulphide.	Stannic sulphide.
	Auric sulphide.
	Platinic sulphide.

Cupric sulphide is slightly soluble in ammonium sulphide, insoluble, however, in sodium sulphide and in potassium sulphide. Mercuric sulphide is insoluble in ammonium sulphide, but soluble in sodium sulphide and in potassium sulphide containing free alkali. Stannous sulphide is insoluble in colorless ammonium sulphide, but easily soluble in yellow ammonium sulphide.

To ascertain whether sulphides of both basic and acid divisions or of only one division are present, the precipitate produced by hydrogen sulphide is examined regarding its behavior with ammonium sulphide. For this purpose a small portion of the precipitate in a test-tube is treated with ammonium hydroxide and then with yellow ammonium sulphide and gently warmed, any residue remaining undissolved is filtered off, and the filtrate is acidified with dilute hydrochloric acid, to ascertain whether a sulpho-salt is present in the solution,—that is, whether a (colored) precipitate of sulphide is formed.

If none of the sulphides have gone into solution, and only a milkiness, due to the separation of sulphur from the yellow ammonium sulphide, is produced on the addition of the hydrochloric acid, basic sulphides only are present, and the remainder of the precipitate should be treated according to directions given under A, page 132.

If the precipitate is completely dissolved, acid sulphides only are present, and the remainder of the precipitate should be examined according to B, page 132.

If a portion of the precipitate remain undissolved and another portion enter into solution, the entire remainder of the precipitate is treated with ammonium hydroxide and ammonium sulphide, the insoluble part filtered off and examined according to A, while the solution (filtrate) is treated according to B. (See Table III *a*, page 132.)

TABLE III*a*.—SEPARATION OF THE SECOND GROUP.

The precipitate produced by hydrogen sulphide, which may contain
PbS, HgS, CuS, Bi_2S_3, CdS and As_2S_3, Sb_2S_3, Sb_2S_5, SnS, SnS_2,
is gently warmed with ammonium hydroxide and yellow ammonium sulphide and then filtered.

<table>
<tr><td colspan="4">A. Insol. Residue.
PbS, HgS, CuS, Bi_2S_3, CdS.
Boil the residue with dilute nitric acid and then filter:</td></tr>
<tr><td rowspan="3">Insol. Residue.
HgS.
Dissolve by warming with nitro-hydrochloric acid; add $SnCl_2$: white prec. of Hg_2Cl_2 or gray Hg indicates presence of mercury.</td><td colspan="3">Filtrate.
Pb, Bi, Cu, Cd
(as nitrates).
Add dilute H_2SO_4 and then filter.</td></tr>
<tr><td rowspan="2">Precipitate,
white:
$PbSO_4$
indicates presence of lead.</td><td colspan="2">Filtrate.
Bi, Cu, Cd, as nitrates.
Add NH_4OH:</td></tr>
<tr><td>Precipitate,
white:
$BiO\text{-}OH$.
Dissolve in HCl and add the solution to water: separation of white $BiOCl$ indicates presence of bismuth.</td><td>Filtrate:
Cu and Cd.
Cu: recognized by the blue color of the liquid.
Cd: add KCN and pass H_2S into the solution: yellow prec. of CdS indicates presence of cadmium.</td></tr>
</table>

<table>
<tr><td colspan="2">B. Filtrate.
As_2S_5, Sb_2S_5, SnS_2 (as sulpho-salts); precipitate the sulphides with HCl and collect on a filter. If on adding HCl only a milkiness or a white prec. is produced, none of the sulphides of this group were dissolved by the $(NH_4)_2S$.
(a) Separation by means of Hydrochloric Acid.
The prec. is warmed with conc. HCl, the solution diluted with water and filtered.</td></tr>
<tr><td>Insol. Residue.
As_2S_5, yellow.
Oxidize with HNO_3, evaporate to dryness, dissolve residue in water, add magnesia mixture: white, crystalline prec. ($MgNH_4AsO_4$) indicates presence of arsenic.</td><td>Filtrate.
$SbCl_3$, $SnCl_4$.
Sb: treat with zinc on platinum foil: production of a black adherent coating on the foil indicates presence of antimony (7, page 31).
Sn: precipitate the tin with zinc, filter and dissolve the prec. in HCl; add $HgCl_2$: white prec. of Hg_2Cl_2 or gray Hg indicates presence of tin (5, page 34).</td></tr>
<tr><td colspan="2">(b) Separation by means of Ammonium Carbonate.
The precipitate of sulphides is digested with a conc. solution of $(NH_4)_2CO_3$ and filtered.</td></tr>
<tr><td>Filtrate.
As_2S_5.
Evaporate to dryness on a water-bath, oxidize the residue with conc. HNO_3, evaporate to dryness, dissolve in water, and add magnesia mixture: white cryst. prec. ($MgNH_4AsO_4$) indicates presence of arsenic.</td><td>Insol. Residue.
Sb_2S_5, SnS_2.
Dissolve in HCl and test with zinc, etc., as above described.</td></tr>
</table>

TABLE III *b*.—SEPARATION OF THE ACID SULPHIDES (SULPHO-SALTS) OF THE SECOND GROUP.

If the presence of gold or platinum is suspected,

The ammon. sulphide solution is treated with HCl to precipitate the sulphides. (The production of only a milkiness or a white prec. of sulphur from the ammon. sulphide indicates the absence of sulphides of this group.) The precipitate, which may contain

As_2S_5, Sb_2S_5, SnS, SnS_2, Au_2S_3, PtS_2,

is collected on a filter, dried, and then mixed with twice its bulk of a dry mixture consisting of equal parts of Na_2CO_3 and KNO_3. This mixture is introduced in small portions at a time into a porcelain crucible containing two parts of KNO_3 (compared with the quantity of precipitate), which is kept just at the point of fusion. When cool, the fused mass is extracted with water containing alcohol and filtered.

<table>
<tr><td colspan="4">Insol. Residue.
Au, Pt, SnO_2, $Na_2H_2Sb_2O_7$.
Boil with conc. NaOH, dilute with water, and filter.</td><td rowspan="4">Filtrate.
Na_3AsO_4.
Evaporate the alcohol, add magnesia mixture: white, cryst. prec. of $MgNH_4AsO_4$ indicates presence of arsenic.</td></tr>
<tr><td colspan="3">Insol. Residue.
Au, Pt, $Na_2H_2Sb_2O_7$.
Boil with conc. HCl, dilute with water, and filter.</td><td rowspan="3">Filtrate.
$SnO(ONa)_2$.
Acidulate with HCl, concentrate by evaporation, precipitate with zinc, filter, and dissolve the prec. in HCl, add $HgCl_2$: white prec. of Hg_2Cl_2 or gray Hg indicates presence of tin (5, page 34).</td></tr>
<tr><td colspan="2">Insol. Residue.
Au, Pt.
Dissolve in nitro-hydrochloric acid, evaporate to dryness on water-bath, dissolve residue in water, boil with $FeSO_4$, and filter.</td><td rowspan="2">Filtrate.
$SbCl_3$.
Treat with zinc on platinum foil: production of a black adherent coating on the foil indicates presence of antimony (7, page 31).</td></tr>
<tr><td>Insol. Residue.
Gold.
Yellow globule when fused on charcoal.</td><td>Filtrate.
$PtCl_4$.
Pass H_2S into the hot solution, filter, dissolve precip. in nitro-hydrochloric acid, evap. to dryness on water-bath, dissolve residue in water, place in a watch-glass, add NH_4Cl, and stir with a glass rod: yellow cryst. precip. of $(NH_4Cl)_2PtCl_4$ indicates presence of platinum.</td></tr>
</table>

A. FURTHER SEPARATION OF THE BASIC SULPHIDES.

The thoroughly washed precipitate of the basic sulphides is taken from the filter, placed in a porcelain dish, and boiled with dilute nitric acid (adding fresh portions of water to replace that lost by evaporation) until no further change takes place in the precipitate. Lead, bismuth, copper, and cadmium enter into solution; mercuric sulphide remains insoluble as a heavy black powder. The mercuric sulphide is collected on a filter, washed, and then dissolved in nitro-hydrochloric acid, which converts it into $HgCl_2$. After evaporating the excess of acid and diluting with water, this solution yields with stannous chloride a white precipitate of Hg_2Cl_2 or a gray precipitate of metallic mercury.

If the precipitate of sulphides is completely dissolved by the dilute nitric acid (with the exception of sulphur, which floats on the surface of the liquid), mercury was not present. White $PbSO_4$ (see 4 and 6, page 14) as well as white $Hg_3S_2(NO_3)_2$ (see 4, page 12) may be precipitated with the mercuric sulphide.

The excess of acid is evaporated from the nitric acid solution obtained as above described, the solution diluted with a small quantity of water, and then treated with dilute sulphuric acid: lead is precipitated as white plumbic sulphate. The plumbic sulphate is filtered off, and the filtrate treated with ammonium hydroxide. If bismuth is present a white precipitate of BiO–OH, bismuth hydroxide, insoluble in an excess of the reagent, is produced. As a confirmatory test the precipitate should be collected on a filter and dissolved in dilute hydrochloric acid; if, on adding the solution to a large quantity of water, a separation of white bismuth oxychloride takes place, the presence of bismuth is fully established. Copper and cadmium are also precipitated by ammonium hydroxide, but redissolve in an excess of the reagent. If the

solution is colored blue, copper is present. To test for cadmium the solution is decolorized by potassium cyanide, and hydrogen sulphide conducted into the liquid; a yellow precipitate of CdS indicates the presence of cadmium. If the ammoniacal solution is colorless, it is treated directly with hydrogen sulphide to ascertain whether a precipitate of yellow cadmium sulphide is produced.

(As plumbic sulphate is soluble in concentrated nitric acid and also in salts of ammonium, it might be overlooked in the presence of an excess of nitric acid or in consequence of the incomplete elimination of ammonium sulphide (before dissolving in nitric acid), and thus interfere with the tests for other substances. At the point where bismuth is precipitated by ammonium hydroxide, ferric hydroxide, aluminium hydroxide, etc., may also be precipitated, especially if the original precipitate produced by hydrogen sulphide has not been sufficiently washed. With copper may be found nickel and cobalt; with cadmium, zinc. Plumbic hydroxide might also be precipitated here by ammonium hydroxide.)

B. FURTHER SEPARATION OF ACID SULPHIDES.

The ammonium sulphide solution may contain the sulpho-salts $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$, and may yield on the addition of hydrochloric acid a yellow or orange-red precipitate of As_2S_5, Sb_2S_5, SnS_2. If only a milkiness or a white precipitate, due to the separation of sulphur from the ammonium sulphide, is produced, it indicates the absence of sulphides of arsenic, antimony, and tin. (Any black SnS which may have been present originally would be precipitated here as yellow SnS_2; see 1, page 33.) The colored precipitate is collected on a filter and thoroughly washed. The separation of the three sulphides may be accomplished by either of two methods,—by hydrochloric acid or by ammonium carbonate.

The separation by ammonium carbonate is preferable in case the preliminary examination indicates the presence of arsenic.

1. *Separation by Hydrochloric Acid.*—The precipitate of sulphides, obtained by the addition of hydrochloric acid to the ammonium sulphide solution (after being pressed between sheets of filter paper to remove the excess of moisture), is treated with concentrated hydrochloric acid and warmed: antimony and tin enter into solution as chlorides, while arsenic sulphide and sulphur remain undissolved. (Cupric sulphide would also be dissolved by the hydrochloric acid. A test for it may be made by treating a few drops of the solution with ammonium hydroxide; the production of a blue coloration indicates the presence of copper.)

To test for antimony, a few drops of the hydrochloric acid solution are placed on platinum foil and a small piece of zinc is placed in the liquid. If antimony is present, a black deposit of metallic antimony is formed which adheres to the platinum foil. To test for tin which may be present as stannic chloride, a fragment of metallic zinc is placed in the remainder of the hydrochloric acid solution; if both tin and antimony are present, they are precipitated as a spongy metallic mass. When the precipitation is complete, the supernatant liquid containing zinc chloride is poured off and the metallic powder remaining is treated with moderately concentrated hydrochloric acid, which dissolves the tin as stannous chloride, leaving the antimony undissolved. The antimony is removed by filtration, and the solution of stannous chloride thus obtained yields with mercuric chloride a precipitate of either white mercurous chloride or of gray metallic mercury (see 4, page 33). On dissolving the sulphides in hydrochloric acid, arsenic sulphide (together with sulphur) remains undissolved. To confirm the presence of arsenic, the arsenic sulphide is dissolved in warm concentrated nitric acid, the solu-

tion evaporated to dryness on a water-bath, and the residue, containing arsenic acid, dissolved in water. Ammonium chloride, ammonium hydroxide, and magnesium sulphate are then added, to ascertain whether crystalline $MgNH_4AsO_4$, ammonium magnesium arseniate, is precipitated. The precipitate is always crystalline; in very dilute solutions it forms only after standing some time.

2. *Separation by Ammonium Carbonate.*—If the precipitate is supposed to contain much arsenic sulphide, it is thoroughly washed with water and then digested with a concentrated solution of ammonium carbonate. Arsenic sulphide enters into solution (see page 22), while Sb_2S_5, antimonic sulphide, and SnS_2, stannic sulphide, remain undissolved, and after being collected on a filter and washed are dissolved in hydrochloric acid and separated according to 1, page 136. The ammonium carbonate solution of arsenic sulphide is evaporated to dryness on a water-bath, and the residue treated with concentrated nitric acid to oxidize the arsenic to arsenic acid. The solution is again evaporated to dryness, dissolved in water, and precipitated with magnesia mixture as $MgNH_4AsO_4$, as described above. (To determine whether the arsenic, antimony, or tin existed in the *ic* or *ous* condition, see the pages treating of the special reactions of these metals. It is, of course, understood that, in testing for arsenic acid in the presence of phosphoric acid, hydrogen sulphide is the only reagent that can be employed.)

C. FURTHER SEPARATION OF ACID SULPHIDES IF THE PRESENCE OF GOLD OR PLATINUM IS SUSPECTED.

The ammonium sulphide solution may contain the sulphosalts $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$, $(NH_4)_3AuS_3$, $(NH_4)_2PtS_3$, and may yield on the addition of hydrochloric acid a yellow, orange-red, or brownish-black precipitate of

As_2S_5, Sb_2S_5, SnS_2, Au_2S_3, PtS_2. If only a milkiness or a white precipitate is produced on adding the hydrochloric acid (due to the separation of sulphur from the ammonium sulphide), it indicates the absence of sulphides of arsenic, antimony, tin, gold, and platinum. The colored precipitate is collected on a filter, thoroughly washed, dried, and then mixed with twice its bulk of a dry mixture consisting of equal parts of sodium carbonate and potassium nitrate. This mixture is introduced, in small portions at a time, into a porcelain crucible containing two parts (compared with the quantity of precipitate) of potassium nitrate, which is kept just at the point of fusion. The temperature must not be of such a degree as to decompose the potassium nitrite resulting from the fusion of the potassium nitrate, as, when the precipitate is added, sodium stannate instead of stannic oxide may be formed. When cool, the fused mass is extracted with water containing alcohol and filtered. The alcohol is evaporated from the filtrate, which may contain arsenic, and then ammonium hydroxide, ammonium chloride, and magnesium sulphate are added. A white crystalline precipitate of ammonium magnesium arseniate, which may appear immediately or after some time, indicates the presence of arsenic.

The insoluble residue, which may contain metallic gold and platinum, stannic oxide, and sodium pyroantimonate, is boiled with a concentrated solution of sodium hydroxide, diluted with water, and filtered. The filtrate, which may contain tin as sodium stannate, is acidulated with hydrochloric acid, concentrated by evaporation, and a piece of metallic zinc placed in the solution to precipitate the tin. The precipitate is collected on a filter, dissolved in hydrochloric acid, and mercuric chloride added to the solution. The production of a white precipitate of mercurous chloride or of gray metallic mercury indicates the presence of tin.

The residue, insoluble in sodium hydroxide, which may contain gold, platinum, and sodium pyroantimonate, is boiled with concentrated hydrochloric acid, slightly diluted with water, and then filtered. A portion of the filtrate, which may contain antimonious chloride, is placed on platinum foil and a fragment of metallic zinc placed in it. The production on the platinum of a brown or black adherent coating indicates the presence of antimony.

The residue insoluble in concentrated hydrochloric acid, which may contain metallic gold and platinum, is dissolved by heating with nitro-hydrochloric acid, the solution evaporated to dryness on a water-bath, the residue dissolved in water, and the solution boiled with ferrous sulphate and then filtered. The insoluble residue of gold on the filter is fused on charcoal with the blowpipe to obtain the gold in the form of a yellow metallic globule.

The filtrate, which may contain platinic chloride, is heated, and, while hot, hydrogen sulphide is passed into the solution. The precipitate is collected on a filter, dissolved by heating with nitro-hydrochloric acid, and evaporated to dryness on a water-bath. The residue is dissolved in a small quantity of water, placed in a watch-glass, ammonium chloride added, and the liquid stirred with a glass rod. A yellow, crystalline precipitate of ammonium platinic chloride indicates the presence of platinum.

SEPARATION OF THE THIRD GROUP.

The tests for phosphates and for oxalates need be made in this group only when the original substance was dissolved in acids or when solutions having an acid reaction are presented for analysis.

The precipitate produced by ammonium hydroxide, after being washed, is warmed with just sufficient dilute hydro-

chloric acid to dissolve it, the solution cooled, and sodium hydroxide added in excess. (To determine whether sodium hydroxide is present in excess, a drop of the solution is rubbed between the fingers, a slippery sensation is felt in case the alkali is in excess; the reaction with turmeric or litmus paper is in this case of no value, as $Al_2O_2(ONa)_2$ and $Cr_2O_2(ONa)_2$, which may be formed here, are also alkaline in reaction.) Chromium hydroxide dissolves in the sodium hydroxide, imparting a green color to the solution; aluminium hydroxide and aluminium phosphate dissolve without imparting a color; the remaining oxides and salts are precipitated by sodium hydroxide in the same manner as by ammonium hydroxide. In the presence of iron, chromium also may be precipitated.

TABLE IV.—SEPARATION OF THE THIRD GROUP,—A.

The precipitate, containing Fe, Cr, Al, Mn, as hydroxides,
Fe, Al, Ba, Sr, Ca, Mg, as phosphates,
Ba, Sr, Ca (and Mg), as oxalates,
is treated with an excess of sodium hydroxide and filtered.

<table>
<tr><td colspan="2">Filtrate.
Cr, Al, H_3PO_4.
Cr: green solution; boil: a dirty-green precipitate of $Cr_2(OH)_6$ indicates the presence of chromium.
Al: colorless solution; or the filtrate from the precipitate of $Cr_2(OH)_6$ is divided into two portions:</td><td rowspan="2">Precipitate.
The remaining bases of the group.
Test for phosphoric acid and oxalic acid according to page 141, b, and then separate the bases according to Table V., page 142.</td></tr>
<tr><td>First portion,—treat with ammonium chloride: a white precipitate of $Al_2(OH)_6$ or $Al_2(PO_4)_2$ indicates the presence of Al.</td><td>Second portion,—treat with nitric acid and ammonium molybdate: a yellow precipitate indicates the presence of phosphoric acid.</td></tr>
</table>

(*a*) If the sodium hydroxide solution is emerald-green in color, it contains chromium as $Cr_2O_2(ONa)_2$, sodium chromite,

which is precipitated by boiling as chromium hydroxide. The filtrate from the chromium hydroxide or the originally colorless solution may contain aluminium hydroxide and phosphoric acid. A portion of the solution is tested for aluminium by the addition of ammonium chloride: if aluminium is present a white, gelatinous precipitate of aluminium hydroxide or aluminium phosphate (if phosphoric acid is present) is produced. Another portion of the solution is acidulated with nitric acid, then gently warmed, and tested with ammonium molybdate for phosphoric acid. A yellow precipitate of $(NH_4)_3PO_4(MoO_3)_{10}$, ammonium phosphomolybdate, indicates the presence of phosphoric acid (see 6, page 65).

(*b*) The precipitate obtained on the addition of sodium hydroxide (in case the original substance was dissolved in acids or the solution presented for analysis had an acid reaction) is tested for phosphoric and oxalic acids. If these acids are absent, the precipitate is treated directly according to IV., pages 145 and 146.

A small portion of the precipitate is dissolved in dilute nitric acid and the solution divided into two portions. To one portion concentrated nitric acid and ammonium molybdate are added. If phosphoric acid is present, a yellow precipitate of ammonium phosphomolybdate will be formed, either immediately or after standing some time.

The second portion is boiled with sodium carbonate, which precipitates the bases as hydroxides and carbonates, while the oxalic acid enters into solution as sodium oxalate; for example:

$$CaC_2O_4 + Na_2CO_3 = CaCO_3 + Na_2C_2O_4.$$

The liquid is filtered, and the filtrate acidified with acetic acid, then gently heated to completely expel carbon dioxide, and finally tested with calcium chloride for oxalic acid. If

oxalic acid is present, a white precipitate of calcium oxalate is produced.

The remainder of the precipitate produced by the sodium hydroxide is now examined according to I.
if both *phosphoric* and *oxalic acids* are present;

according to II.
if *phosphoric acid* is present and *oxalic acid* is absent;

according to III.
if *phosphoric acid* is absent and *oxalic acid* is present;

according to IV.
if both *phosphoric* and *oxalic acids* are absent.

TABLE V.—SEPARATION OF THE THIRD GROUP,—B.

I. *Separation if both Phosphoric and Oxalic Acids are Present.*

Boil the nitric acid solution of the precipitate with tin foil to precipitate phosphoric acid, filter, boil the filtrate with excess of Na_2CO_3, filter, dissolve the precipitate in HNO_3, add NH_4Cl and NH_4OH to the solution, and filter:

<table>
<tr>
<td colspan="2">Precipitate.
Cr, Fe, Mn.
Fuse with Na_2CO_3 and KNO_3, extract the mass with hot water: a yellow filtrate indicates presence of Cr. Filter, dissolve residue in HCl, add $NaC_2H_3O_2$, boil, and filter:</td>
<td colspan="2">Filtrate.
Mn, Ba, Sr, Ca, Mg as nitrates.
Add $(NH_4)_2S$, and filter:</td>
</tr>
<tr>
<td>Precipitate.
Brownish-red $Fe_2(OH)_4(C_2H_3O_2)_2$ indicates presence of iron.</td>
<td>Filtrate.
Add $(NH_4)_2S$: pale-salmon-colored MnS indicates presence of manganese.</td>
<td>Precipitate.
Pale - salmon-colored MnS indicates presence of manganese. (Compare Group IV., page 146.)</td>
<td>Filtrate.
Test according to Groups V. (page 148) and VI. (page 152) for Ba, Sr, Ca, and Mg.</td>
</tr>
</table>

II. *Separation if Phosphoric Acid is Present and Oxalic Acid is Absent.*

Boil the nitric acid solution of the precipitate with tin foil to precipitate phosphoric acid, filter, to the filtrate add NH_4Cl and NH_4OH, filter:

<table>
<tr>
<td colspan="2">Precipitate.
Cr, Fe, Mn.
Fuse with Na_2CO_3 and KNO_3, extract the mass with hot water, filter: a yellow filtrate indicates presence of Cr. Dissolve residue in HCl, add $NaC_2H_3O_2$, boil, and filter:</td>
<td colspan="2">Filtrate.
Mn, Ba, Sr, Ca, and Mg.
Add $(NH_4)_2S$ and filter.</td>
</tr>
<tr>
<td>Precipitate.
Brownish-red $Fe_2(OH)_4(C_2H_3O_2)_2$ indicates presence of iron.</td>
<td>Filtrate.
Add $(NH_4)_2S$: pale-salmon-colored MnS indicates presence of manganese. (Compare Group IV., page 146.)</td>
<td>Precipitate.
Pale - salmon-colored MnS indicates presence of manganese. (Compare Group IV., page 146.)</td>
<td>Filtrate.
Test according to Groups V. (page 148) and VI. (page 152) for Ba, Sr, Ca, and Mg.</td>
</tr>
</table>

III. *Separation if Phosphoric Acid is Absent and Oxalic Acid is Present.*

Boil the precipitate, obtained by treatment with NaOH, with Na_2CO_3, filter, dissolve the precipitate in HNO_3, add NH_4Cl and NH_4OH, filter:

<table>
<tr>
<td colspan="2">Precipitate.
Cr, Fe, Mn.
Fuse with Na_2CO_3 and KNO_3, extract the mass with hot water, filter: a yellow filtrate indicates presence of Cr. Dissolve residue in HCl, add $NaC_2H_3O_2$, boil, and filter:</td>
<td rowspan="2">Filtrate.
Test according to Groups V. (page 148) and VI. (page 152) for Ba, Sr, Ca, and Mg.</td>
</tr>
<tr>
<td>Precipitate.
Brownish-red $Fe_2(OH)_4(C_2H_3O_2)_2$ indicates presence of iron.</td>
<td>Filtrate.
Add $(NH_4)_2S$: pale-salmon-colored MnS indicates presence of manganese. (Compare Group IV., page 146.)</td>
</tr>
</table>

IV. *Separation if both Phosphoric and Oxalic Acids are Absent.*

Fuse the precipitate, obtained by treatment with NH_4Cl and NH_4OH (which may contain Cr, Fe, and Mn), with Na_2CO_3 and KNO_3, extract the mass with hot water, filter: a yellow filtrate indicates presence of Cr. Dissolve residue in HCl, add $NaC_2H_3O_2$, boil, and filter:

Precipitate.	*Filtrate.*
Brownish-red $Fe_2(OH)_4(C_2H_3O_2)_2$ indicates presence of iron.	Add $(NH_4)_2S$: pale-salmon-colored MnS indicates presence of manganese. (Compare Group IV., page 146.)

I. If both phosphoric acid and oxalic acid are present, the remainder of the precipitate is dissolved in concentrated nitric acid and the solution heated with an excess of tin foil. The stannic hydroxide which is produced precipitates the phosphoric acid as stannic phosphate:

$$3Sn(OH)_4 + 4H_3PO_4 = Sn_3(PO_4)_4 + 12H_2O.$$

The precipitated mixture of stannic hydroxide and stannic phosphate is filtered off, and the residue repeatedly washed with hot water (to dissolve the nitrates which are soluble with difficulty in concentrated nitric acid), and the filtrate is then tested with ammonium molybdate to determine whether the phosphoric acid has been completely precipitated. If the phosphoric acid was not completely precipitated, the treatment with tin foil must be repeated.

The filtrate, free from phosphoric acid, is boiled with an excess of sodium carbonate; oxalic acid enters into solution, while the bases are precipitated as hydroxides and carbonates. This precipitate is collected on a filter and then dissolved in nitric acid, and the solution treated with ammonium chloride and ammonium hydroxide. Phosphoric acid and oxalic acid having been removed, only iron, chromium, and manganese are precipitated (as hydroxides), and are to be separated ac-

cording to Table IV., page 140. The filtrate[1] from any precipitate that may have formed is to be tested according to Groups IV., V., and VI., for manganese, barium, strontium, calcium, and magnesium.

II. If phosphoric acid is present and oxalic acid is absent, the phosphoric acid is removed as above described (I.) by nitric acid and tin, the precipitate is then filtered off, and the filtrate treated with ammonium chloride and ammonium hydroxide to precipitate iron, chromium, and magnesium. This precipitate is collected on a filter, separated according to Table IV., page 140, and the filtrate tested according to Groups V. and VI. for manganese, barium, strontium, calcium, and magnesium.

III. If phosphoric acid is absent and oxalic acid is present, the remainder of the precipitate obtained by treatment with sodium hydroxide is boiled with sodium carbonate, whereby the oxalic acid enters into solution. The residue containing the bases is filtered off, thoroughly washed, and dissolved in nitric acid. Ammonium chloride and ammonium hydroxide are then added to precipitate iron, chromium, and manganese, which are collected on a filter and separated according to Table IV., page 140. The filtrate is tested according to Group V. for barium, strontium, and calcium.[2]

IV. The precipitate, which may contain chromium, iron, and manganese, is first examined for chromium. For this purpose a small portion of the precipitate is fused on platinum foil with sodium carbonate and potassium nitrate, and the fused mass extracted with a small quantity of hot water. If the solution is yellow in color (due to potassium chromate),

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[1] If the tin foil contain copper, the filtrate will be blue in color.

[2] Traces of magnesium may be found here; the filtrate from Group V. should be tested for it according to the directions given under Group VI.

chromium is present. If chromium is present, the remainder of the precipitate is fused in a crucible with sodium carbonate aud potassium nitrate, and, after cooling, the mass is treated with water to dissolve the potassium chromate. The residue, which may contain iron and manganese as oxides, should be examined as follows:[1]

To separate iron from manganese, the remainder of the precipitate (if chromium is absent) or the residue (left after extracting the potassium chromate with water) is dissolved in the least possible quantity of hydrochloric acid, and treated with sodium acetate until the yellow color of the liquid (due to Fe_2Cl_6) is changed to claret-red (due to $Fe_2(C_2H_3O_2)_6$). After the solution is sufficiently diluted, it is heated to boiling: iron is precipitated as $Fe_2(OH)_4(C_2H_3O_2)_2$, basic ferric acetate, which is then filtered off, while the manganese remains in solution. The latter is precipitated in the filtrate by ammonium sulphide as pale-salmon-colored manganous sulphide.

SEPARATION OF THE FOURTH GROUP.

After washing the precipitate, while on the filter, with water containing hydrogen sulphide, the filter is pierced with a glass rod and the precipitate washed with cold dilute hydrochloric acid into a beaker placed below. Manganous

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[1] If manganese is present, green potassium manganate is formed in the fusion; on extracting the fused mass with water, purplish-red potassium permanganate is formed, together with insoluble brown $MnO(OH)_2$:

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + MnO(OH)_2 + 4KOH.$$

If the resulting solution is purplish red in color, in order to test for chromium the remainder of the precipitate is dissolved in hydrochloric acid. Chlorine is driven off by boiling, ammonium chloride and ammonium hydroxide are added and the resulting precipitate is quickly collected on a filter. The precipitate obtained will then be sufficiently free from manganese to be again tested for chromium, etc., as above described.

sulphide and zinc sulphide are dissolved by the dilute hydrochloric acid as manganous chloride and zinc chloride, while nickelous sulphide and cobaltous sulphide remain undissolved. The nickelous and cobaltous sulphides are collected on a filter and washed with water containing hydrogen sulphide.

TABLE VI.—SEPARATION OF THE FOURTH GROUP.

The precipitate, which may contain MnS, ZnS, NiS, CoS, is treated with cold dilute hydrochloric acid and filtered:

<table>
<tr><td colspan="2">Insol. Residue.
NiS, CoS.
Dissolve in nitro-hydrochloric acid, evaporate excess of acid, neutralize remainder with NaOH, add $HC_2H_3O_2$ in excess and then $NaC_2H_3O_2$ and KNO_2:</td><td colspan="2">Filtrate.
$ZnCl_2$, $MnCl_2$.
Heat to drive off H_2S, add excess of NaOH, and filter:</td></tr>
<tr><td>Precipitate.
Yellow crystalline $K_6Co_2(NO_2)_{12}$ indicates presence of cobalt.</td><td>Filtrate.
$NiCl_2$.
Add NaOH: pale-apple-green $Ni(OH)_2$ indicates presence of nickel.</td><td>Precipitate.
White $Mn(OH)_2$, rapidly changing to brown $Mn_2(OH)_6$, indicates presence of manganese.</td><td>Filtrate.
$Zn(ONa)_2$.
Treat with H_2S: white ZnS_2 indicates presence of zinc.</td></tr>
</table>

The hydrochloric acid filtrate is warmed until the hydrogen sulphide is completely driven off, and then treated with sodium hydroxide in excess. Manganese is precipitated as white manganous hydroxide, which, when exposed to the air, rapidly changes to brown manganic hydroxide; while zinc, at first precipitated as zinc hydroxide, is dissolved as $Zn(ONa)_2$, sodium zincate. The manganous hydroxide is filtered off, and the alkaline filtrate treated with hydrogen sulphide, which precipitates zinc as white zinc sulphide.

The mixture of nickelous sulphide and cobaltous sulphide

remaining on the filter, insoluble in hydrochloric acid, is dissolved by heating with nitro-hydrochloric acid. The greater part of the excess of acid is driven off by boiling, and the solution neutralized by adding sodium hydroxide drop by drop until a permanent precipitate of hydroxides is formed. Acetic acid in excess and sodium acetate are then added, followed by the addition of an excess of a concentrated solution of potassium nitrite. If cobalt is present, a yellow crystalline precipitate of potassium cobaltic nitrite is formed, either immediately or after standing some time. After several hours the precipitate is filtered off, and the filtrate treated with sodium hydroxide; the formation of a pale-apple-green precipitate of nickelous hydroxide indicates the presence of nickel. (The precipitate of nickel should be tested in the bead of microcosmic salt; see 7, page 49.)

SEPARATION OF THE FIFTH GROUP.

FIRST METHOD.

The precipitate, consisting of carbonates, is dissolved in hydrochloric acid, which converts the carbonates into chlorides. Only a small quantity of hydrochloric acid is used, so that the solution may be concentrated but only slightly acid. A small portion of the solution of chlorides is treated with a concentrated solution of calcium sulphate.

TABLE VII.—SEPARATION OF THE FIFTH GROUP, FIRST METHOD.

The precipitate, which may contain $BaCO_3$, $SrCO_3$, $CaCO_3$, is dissolved in a small quantity of HCl, and a portion of the solution treated with $CaSO_4$:

<table>
<tr>
<td rowspan="3">No precipitate is produced:
Ba and Sr
are absent. Treat the remainder of the HCl solution with NH_4OH and $(NH_4)_2C_2O_4$: white precipitate, CaC_2O_4, indicates presence of calcium.</td>
<td colspan="3">A white precipitate is produced.
Evaporate the remainder of the HCl solution to dryness on a water-bath, pulverize the residue, extract with strong alcohol, and filter:</td>
</tr>
<tr>
<td rowspan="2">Insol. Residue.
$BaCl_2$.
Place a portion on platinum wire and hold in the flame:
a green color imparted to the flame indicates presence of barium.</td>
<td colspan="2">Filtrate.
$SrCl_2$, $CaCl_2$.
Evaporate to dryness on a water-bath, evaporate residue twice to dryness with conc. HNO_3, extract the residue with strong alcohol, and filter:</td>
</tr>
<tr>
<td>Insol. Residue.
$Sr(NO_3)_2$.
Place a portion on platinum wire and hold in the flame:
a crimson color imparted to the flame indicates presence of strontium.</td>
<td>Filtrate.
$Ca(NO_3)_2$.
Evaporate until free from alcohol, add NH_4OH and $(NH_4)_2C_2O_4$: white precipitate, CaC_2O_4, indicates presence of calcium.</td>
</tr>
</table>

(*a*) If upon the addition of the calcium sulphate no precipitate is formed, either immediately or after standing some time, barium and strontium are absent. The remainder of the hydrochloric acid solution (to which calcium sulphate has not been added) is treated with ammonium hydroxide and ammonium oxalate, when, if calcium is present, a white precipitate of calcium oxalate is formed.

(*b*) If on the addition of calcium sulphate a white precipitate is immediately produced, barium is probably present; if

a turbidity appear after some time, probably strontium only is present. In either case the remainder of the hydrochloric acid solution (which has not been treated with calcium sulphate) is evaporated to dryness on a water-bath, and the residue pulverized and extracted with strong alcohol. Barium chloride remains undissolved, while strontium chloride and calcium chloride enter into solution. The liquid is filtered through a dry[1] filter, and a portion of the residue on the filter is placed on a platinum wire and held in the Bunsen flame; a green color imparted to the flame indicates the presence of barium. The alcoholic filtrate is evaporated on a water-bath to ascertain (by a residue remaining) whether anything has entered into solution. Any residue (consisting of chlorides) remaining is evaporated twice to dryness with an excess of concentrated nitric acid (free from chlorine), which converts the chlorides into nitrates:

$$SrCl_2 + 2HNO_3 = Sr(NO_3)_2 + 2HCl,$$

and the residue of nitrates is then extracted with strong alcohol as before described; calcium nitrate enters into solution, while strontium nitrate, which remains undissolved, is collected on a filter, and a portion placed on a platinum wire and held in the Bunsen flame; a crimson color imparted to the flame indicates the presence of strontium. The alcoholic filtrate is now evaporated until free from alcohol, and any traces of strontium and barium are precipitated with a few drops of sulphuric acid,[2] and the liquid is filtered and tested for calcium with ammonium hydroxide and ammonium oxalate. The formation of a white precipitate indicates the presence of calcium.

---

[1] A filter which has not been moistened with water.

[2] From concentrated solutions calcium also may be partly precipitated, although, because of its solubility, a considerable quantity of calcium sulphate remains in solution.

SECOND METHOD.

The precipitate, consisting of carbonates, is dissolved in a small quantity of acetic acid, and a small portion of the solution is tested for barium with potassium chromate.

TABLE VIII.—SEPARATION OF THE FIFTH GROUP, SECOND METHOD.

The precipitate, which may contain $BaCO_3$, $SrCO_3$, $CaCO_3$, is dissolved in a small quantity of acetic acid, and a portion of the solution treated with potassium chromate:

<table>
<tr>
<td colspan="3">A yellow precipitate is produced:
$BaCrO_4$,
indicating the presence of barium.
Treat the remainder of the acetic acid solution with potassium chromate to precipitate the barium, filter, add NH_4OH and $(NH_4)_2CO_3$ to the filtrate, and boil:</td>
<td colspan="2">No precipitate is produced:
Ba
is absent.
A portion of the solution is tested for Sr with $CaSO_4$:</td>
</tr>
<tr>
<td rowspan="2">No precipitate is produced: Ca and Sr are absent.</td>
<td colspan="2">A precipitate is produced.
Collect the precipitate on a filter, dissolve the precipitate in a small quantity of HCl, and test a portion of the solution for Sr with $CaSO_4$:</td>
<td rowspan="2">No precipitate is produced:
Sr
is absent.
Treat the remainder of the acetic acid solution with NH_4OH and $(NH_4)_2C_2O_4$: white precipitate,
CaC_2O_4,
indicates presence of calcium.</td>
<td rowspan="2">A precipitate is produced:
Sr
is present.
Treat the remainder of the acetic acid solution with H_2SO_4 to precipitate Sr, filter, and add NH_4OH and $(NH_4)_2C_2O_4$ to filtrate: white precipitate,
CaC_2O_4,
indicates presence of calcium.</td>
</tr>
<tr>
<td>No precipitate is produced:
Sr
is absent.
Treat the remainder of the HCl solution with NH_4OH and $(NH_4)_2C_2O_4$: white precipitate,
CaC_2O_4,
indicates presence of calcium.</td>
<td>A precipitate is produced:
Sr
is present.
Treat the remainder of the HCl solution with H_2SO_4 to precipitate Sr, filter, and add NH_4OH and $(NH_4)_2C_2O_4$ to filtrate: white precipitate,
CaC_2O_4,
indicates presence of calcium.</td>
</tr>
</table>

(*a*) If a yellow precipitate is formed, barium is present. The barium is precipitated from the remainder of the acetic acid solution by potassium chromate. The precipitate is filtered off, ammonium hydroxide and ammonium carbonate

are added to the filtrate, and the liquid is boiled to precipitate strontium and calcium. If no precipitate is formed, strontium and calcium are absent; if a precipitate of carbonates is formed, it is collected on a filter, thoroughly washed, and then dissolved in a small quantity of hydrochloric acid.

The solution of chlorides produced by dissolving the carbonates in hydrochloric acid is divided into two portions, one of which is tested for strontium with calcium sulphate. If a precipitate is not produced immediately or after standing some time, strontium is absent. The other portion of the solution of chlorides is neutralized with ammonium hydroxide and tested for calcium with ammonium oxalate. If, on the addition of calcium sulphate, a precipitate of strontium sulphate is formed (thus showing the presence of strontium), the second portion of the solution of chlorides is treated with sulphuric acid, to precipitate the strontium as sulphate, which is then filtered off and the filtrate tested for calcium with ammonium hydroxide and ammonium oxalate.

(*b*) If no precipitate is formed on the addition of potassium chromate, barium is absent. The remainder of the acetic acid solution is then tested for strontium with calcium sulphate and for calcium with ammonium hydroxide and ammonium oxalate, as described above (*a*).

SEPARATION OF THE SIXTH GROUP.

If barium and calcium were found in the Fifth Group, traces of them may remain in the filtrate from that group, and must be removed before proceeding with the separation of the Sixth Group. For this purpose a few drops of dilute sulphuric acid are added to the filtrate to precipitate the barium, and ammonium hydroxide and ammonium oxalate added to precipitate calcium. If precipitates are formed,

they are removed by filtration. A portion of the solution thus rendered free from barium and calcium, or the filtrate from the Fifth Group which originally contained no barium or calcium, is tested for magnesium with ammonium chloride, ammonium hydroxide, and sodium hydrogen phosphate. If magnesium is present, a white, crystalline precipitate of ammonium magnesium phosphate will appear, either immediately or after standing some time. If magnesium is not present, the remainder of the solution is examined according to I., page 117; if it is present, the solution is to be examined according to II., page 118.

I. The remainder of the solution which does not contain magnesium is placed in a porcelain crucible or dish and evaporated to dryness on a water-bath; it is then gently heated over a free flame until vapors of ammonium salts cease to be evolved. If no residue remain, potassium and sodium are absent; if a residue remain, it is dissolved in the least quantity possible of water, and the concentrated solution divided into two portions.

One portion is placed in a watch-glass, treated with platinic chloride and a small quantity of alcohol, and stirred with a glass rod. If potassium is present, a yellow, crystalline precipitate of potassium platinic chloride will be formed.

TABLE IX*a*.—SEPARATION OF THE SIXTH GROUP.

<table>
<tr>
<td colspan="4">A. Examination for Mg, K, Na, Li.
Test the filtrate from the Fifth Group for traces of Ba with H_2SO_4 and for Ca with NH_4OH and $(NH_4)_2C_2O_4$. If precipitates are produced, remove them by filtration. Test a portion of the solution free from Ba and Ca for Mg with NH_4Cl, NH_4OH, and Na_2HPO_4:</td>
<td rowspan="3">B. Examination for Ammonium.
Treat the original substance or solution with NaOH and boil: the evolution of ammoniacal gas, recognized by its odor, etc., indicates presence of ammonium.</td>
</tr>
<tr>
<td colspan="2">A precipitate is produced: $MgNH_4PO_4$, indicating presence of magnesium.
Evaporate the remainder of the solution to dryness on a water-bath, gently heat residue over a free flame until vapors of ammonium salts cease to be evolved.
Dissolve residue in water and a few drops HCl, boil, add $Ba(OH)_2$, filter, add $(NH_4)_2CO_3$ to filtrate, filter, evaporate filtrate to dryness on water-bath, and gently heat residue over a free flame until vapors of ammonium salts cease to be evolved.
(If lithium has been detected by the flame test, proceed according to the separation under Table IX*b*.)</td>
<td colspan="2">No precipitate is produced.
Evaporate the remainder of the solution to dryness on a water-bath, gently heat residue over a free flame until vapors of ammonium salts cease to be evolved.
(If lithium has been detected by the flame test, proceed according to the separation under Table IX*b*.)</td>
</tr>
<tr>
<td>A residue remains: KCl, NaCl.
Dissolve in small quantity of water and divide into two portions.
To one portion add $PtCl_4$: a yellow, crystalline precipitate, $(KCl)_2PtCl_4$, indicates presence of potassium.
To the other portion add clear, freshly-prepared solution of potassium pyroantimonate: a white, crystalline precipitate, $Na_2H_2Sb_2O_7$, indicates presence of sodium.</td>
<td>A residue does not remain: K and Na are absent.</td>
<td>A residue remains: KCl, NaCl.
Dissolve in small quantity of water and divide into two portions.
To one portion add $PtCl_4$: a yellow, crystalline precipitate, $(KCl)_2PtCl_4$, indicates presence of potassium.
To the other portion add clear, freshly-prepared solution of potassium pyroantimonate: a white, crystalline precipitate, $Na_2H_2Sb_2O_7$, indicates presence of sodium.</td>
<td>A residue does not remain: K and Na are absent.</td>
</tr>
</table>

TABLE IX*b*.—SEPARATION OF THE SIXTH GROUP (IN THE PRESENCE OF LITHIUM.)

K, Na, Li.

If a residue remain (see Table IX*a*.), moisten with conc. HCl, evaporate to dryness on a water-bath, extract residue with a mixture of absolute alcohol and ether, and filter:

Insol. Residue.	*Filtrate.*
KCl, NaCl. Divide into two portions. To one portion add $PtCl_4$: a yellow crystalline precipitate, $(KCl)_2PtCl_4$, indicates presence of potassium. To the other portion add clear, freshly-prepared solution of potassium pyroantimonate: a white, crystalline precipitate, $Na_2H_2Sb_2O_7$, indicates presence of sodium.	LiCl. Evaporate to dryness on a water-bath. Place a portion of the residue on a clean platinum wire and hold in the non-luminous flame: a carmine-red color imparted to the flame indicates presence of lithium.

The second portion is tested for sodium by adding a clear, freshly-prepared solution of potassium pyroantimonate. Sodium salts yield with potassium pyroantimonate, either immediately or after standing some time, a white, crystalline precipitate of sodium pyroantimonate. The solution to be tested for sodium must not be acid in reaction, or flocculent antimonic acid will be precipitated. If acid in reaction, the solution should be exactly neutralized with ammonium hydroxide before making the test with potassium pyroantimonate.

To detect small quantities of potassium and sodium, advantage may be taken of their behavior in the non-luminous flame. Sodium imparts a yellow color, potassium a violet color, to the flame. To detect the potassium flame in the presence of the sodium flame (as the intense yellow sodium flame obscures the weaker violet potassium flame), a piece of blue glass (cobalt glass) or an indigo prism (which absorbs the yellow rays) may be employed. Viewed through blue glass or an indigo prism the potassium flame appears crimson-red in color.

II. If magnesium is present in the solution, it must be removed before the tests for potassium and sodium can be made. For this purpose the solution containing magnesium is evaporated to dryness on a water-bath, and the residue gently heated over a free flame until the vapors of ammonium salts cease to be evolved. The residue is then dissolved in water and a few drops of hydrochloric acid. (The presence of ammonium salts interferes with the precipitation of magnesium ; see 1, page 53. The residue does not completely dissolve in water, as part of the magnesium salts were converted into insoluble basic salts by the heating.)

The solution is heated to the boiling point and barium hydroxide added, whereby magnesium hydroxide is precipitated :

$$MgCl_2 + Ba(OH)_2 = Mg(OH)_2 + BaCl_2.$$

(Any sulphuric acid which might be present would also be precipitated.) The magnesium hydroxide is filtered off, and the filtrate treated with ammonium carbonate to precipitate the barium of the barium chloride as barium carbonate. The barium carbonate is filtered off, the filtrate evaporated to dryness, and the residue gently heated in a porcelain dish or crucible until vapors of ammonium salts cease to be evolved, then dissolved in a small quantity of water and the solution divided into two portions and tested for potassium and sodium as described under I., page 117.

III. If lithium has been detected by the flame test in the residue mentioned in Table IX*a*., the residue is moistened with concentrated hydrochloric acid (which converts the bases into chlorides), and evaporated to dryness on a water-bath. The residue remaining is extracted with a mixture consisting of equal volumes of absolute alcohol and ether. Lithium chloride enters into solution, leaving potassium chloride and sodium chloride undissolved. The liquid is filtered, the fil-

trate evaporated to dryness on a water-bath, and a portion of the residue placed on a platinum wire and held in the non-luminous flame. If lithium is present a carmine-red color will be imparted to the flame.

The residue insoluble in alcohol and ether is dissolved in a small quantity of water and divided into two portions. One portion is placed in a watch-glass, platinic chloride and a few drops of alcohol are added, and the liquid is stirred with a glass rod. If potassium is present a yellow, crystalline precipitate of potassium platinic chloride will be formed. The other portion is placed in a watch-glass and treated with a clear, freshly-prepared solution of potassium pyroantimonate and the liquid stirred with a glass rod. If sodium is present a white, crystalline precipitate of potassium pyroantimonate will be formed.

To test for the presence of ammonium salts, a portion of the original substance or solution presented for analysis is placed in a test-tube, treated with a solution of sodium hydroxide, and boiled. If ammonium salts are present ammoniacal gas will be evolved, which may be recognized by its odor, by its changing turmeric paper, moistened with water, brown, and by its forming white clouds of ammonium acetate when a glass rod moistened with acetic acid is held in the atmosphere containing the gas.

In using turmeric paper in this test care must be taken that the turmeric paper does not come in contact with the sides of the test-tube, as in such case the yellow paper may be changed to brown by sodium hydroxide which may be on the glass. Likewise care must be taken that in the ebullition of the liquid none of it is projected on the turmeric paper.

VI. EXAMINATION FOR ACIDS.

THE examination for acids should always be preceded by the examination for bases and by the preliminary examination. (See pages 90, 91, and succeeding pages.)

The number of acids to be taken into consideration depends upon the number of bases present and upon the results of the preliminary examination. Acids which form insoluble compounds with the bases found in the solution need not be sought for; as, for example, if silver is found in the solution, hydrochloric acid cannot be present, or, if barium is found, it is useless to look for sulphuric acid. In neutral solutions containing heavy metals, only a limited number of acids are to be considered, as most of the salts of the heavy metals are insoluble in water.

In solutions having an acid reaction all the acids are to be considered which, with the bases present, form salts soluble in acid solution. (For solubilities see Properties of the Acids, page 59 and succeeding pages.)

If heavy metals are present they must, in many cases, be removed before proceeding with the tests for acids. When possible, this is accomplished by the addition of an excess of sodium carbonate to the solution, thereby precipitating the metals as carbonates or oxides. The precipitate is filtered off, and the filtrate is divided into two unequal portions. The larger portion is neutralized with nitric acid, and the smaller portion with acetic acid (to be used in testing for nitric acid). It is advisable to gently heat the solution after acidulation, in

order to completely expel carbon dioxide.[1] Stannic oxide and arsenic are removed by precipitating with hydrogen sulphide. In this operation sulphuric acid may result from the oxidation of the hydrogen sulphide. In such cases the original solution should be tested directly for sulphuric acid and hydrochloric acid.

In the examination of solutions having an alkaline reaction, they should be neutralized with nitric acid or acetic acid. In case a precipitate is produced the acid should be added in excess, the precipitate filtered off, and the filtrate neutralized with an alkali. (See page 122, *b*.)

Salts which are insoluble in water are examined for acids by treating them directly (without first dissolving them) with a solution of sodium carbonate. When heated to boiling the acid enters into solution as a sodium salt, while the base remains as an insoluble oxide or carbonate. The liquid is filtered, and the filtrate containing the sodium salts is neutralized with nitric acid or acetic acid as above described.

In examining for acids when fusion is necessary, see the chapter on Solution and Fusion, page 103.

The neutral solution is first examined regarding its behavior with the three group reagents: $BaCl_2$, $Pb(C_2H_3O_2)_2$, and $AgNO_3$.

The acids[2] which produce precipitates with the group reagents and the properties of the precipitates are given in the following table.

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[1] If the carbon dioxide has not been completely expelled, precipitates of carbonates may be produced on the addition of the three group reagents: with barium chloride soluble barium bicarbonate might be formed, which would appear as a precipitate only after boiling.

[2] For a classification of the acids composing the four groups, see page 59 and the succeeding pages; in this classification oxalic acid and tartaric acid belong to the second group, and acetic acid to the fourth group.

TABLE X.—BEHAVIOR OF THE ACIDS

Precipitate in the presence of		$BaCl_2$.
Group I.	*Sulphuric acid:*	white (insoluble in HCl)
	Hydrofluosilicic acid:	white (insoluble in HCl)
Group II.	*Sulphurous acid:*	white (soluble in HCl: with evolution of SO_2)
	Hyposulphurous acid:	white (soluble in large quant. of water; soluble in HCl: with evolution of SO_2 and separation of S)
	Phosphoric acid:	white (soluble in HCl)
	Boric acid:	white (precipitated only in conc. solutions; soluble in HCl)
	Hydrofluoric acid:	white (soluble in HCl)
	Carbonic acid:	white (soluble in HCl: with effervescence)
	Silicic acid:	white (soluble in HCl)
	Arsenious acid:	white (soluble in HCl)
	Arsenic acid:	white (soluble in HCl)
	Chromic acid:	yellow (soluble in HCl)
	Oxalic acid:	white (soluble in HCl)
	Tartaric acid:	white (soluble in HCl)
Group III.	*Hydrochloric acid:*	. . . .
	Hydrobromic acid:	. . . .
	Hydriodic acid:	. . . .
	Hydrocyanic acid:	. . . .
	Hydroferrocyanic acid:	. . . .
	Hydroferricyanic acid:	. . . .
	Sulphydric acid:	. . . .
	Nitrous acid:	. . . .
	Hypochlorous acid:	. . . .
Group IV.	*Nitric acid:*	. . . .
	Chloric acid:	. . . .
	Acetic acid:	. . . .

WITH THE GROUP REAGENTS.

$Pb(C_2H_3O_2)_2$.	$AgNO_3$.
white (insoluble in HNO_3) . . .	. . . .
. . . .	. . . .
white (soluble in HNO_3)	white (soluble in HNO_3; becomes gray on boiling)
white (soluble in HNO_3; with separation of S)	white (soluble in HNO_3; rapidly becomes black)
white (soluble in HNO_3)	yellow (soluble in HNO_3)
white (soluble in excess of reagent; soluble in HNO_3)	white (precipitated only from conc. solutions; soluble in HNO_3; decomposed by water)
white (soluble in HNO_3)	. . . .
white (soluble in HNO_3; with effervescence)	white (soluble in HNO_3; on boiling becomes yellow or brown)
white (soluble in HNO_3)	yellow (soluble in HNO_3)
white (soluble in HNO_3)	yellow (soluble in HNO_3)
white (soluble in HNO_3)	reddish brown (soluble in HNO_3)
yellow (soluble in HNO_3)	purplish red (soluble in HNO_3)
white (soluble in HNO_3)	white (soluble in HNO_3)
white (soluble in HNO_3)	white (soluble in HNO_3; separation of Ag on boiling)
white (crystalline, soluble in hot water)	white (curdy, insoluble in HNO_3)
white (soluble with great difficulty in water)	yellowish white (insoluble in HNO_3)
yellow (crystalline, soluble in hot water)	yellow (insoluble in HNO_3)
white (insoluble in water; soluble in HNO_3)	white (curdy, insoluble in HNO_3)
white (insoluble in HNO_3) . . .	white (insoluble in HNO_3)
. . . .	yellow (insoluble in HNO_3)
black (soluble in HNO_3 on warming)	black (soluble in HNO_5 on warming)
yellow coloration	white (soluble in large quant. of water)
white (becomes brown, due to separation of PbO_2)	white (= AgCl)
. . . .	. . . .
. . . .	. . . .
. . . .	. . . .

In many cases reasonably certain conclusions as to which acids are present may be drawn from the color of the precipitates and from the behavior of the latter with the different solvents, if at the same time it is considered which acids could possibly be present under the existing conditions; for example, if a precipitate soluble in nitric acid is produced by argentic nitrate, the presence of hydrochloric acid, hydrobromic acid, etc., is excluded. If the precipitate produced by barium chloride is insoluble in acids, sulphuric acid or hydrofluosilicic acid must be present.

The presence of the different acids, however, is to be further established as follows:

Sulphuric Acid. (*Sulphates.*)

Sulphates when fused (as in the preliminary examination) with sodium carbonate on charcoal and a portion of the fused mass is placed on a silver coin and moistened with water produce a brownish or black stain on the coin.

Barium chloride produces a white precipitate of barium sulphate, insoluble in acids.

Plumbic acetate produces a white precipitate of plumbic sulphate, soluble in neutral ammonium tartrate.

Tests for sulphuric acid should never be made in solutions which have been treated with hydrogen sulphide, because of the probability of the presence of sulphuric acid resulting from the oxidation of hydrogen sulphide.

Tests for sulphuric acid can be made in acid solutions containing bases.

Hydrofluosilicic Acid. (*Silicofluorides.*)

Hydrofluosilicic acid is not precipitated by plumbic acetate, but is precipitated by potassium nitrate as gelatinous potassium silicofluoride (see 3, page 60).

Sulphurous Acid. (*Sulphites.*)

Sulphites when fused with sodium carbonate on charcoal and a portion of the fused mass is placed on a silver coin and moistened with water produce a brownish or black stain on the coin.

On acidulating a solution of a sulphite with hydrochloric acid, sulphurous anhydride is evolved, which may be recognized by its odor of burning sulphur and by its action upon moistened potassium iodate starch-paste paper, the latter becoming blue, owing to the iodine separated by the sulphurous anhydride from the iodate acting upon the starch.

Argentic nitrate precipitates white argentic sulphite, soluble in nitric acid. On boiling the precipitate with water, it is decomposed, with the separation of finely-divided, gray metallic silver.

To detect sulphurous acid in the presence of hyposulphurous acid, see 6, page 62.

Hyposulphurous Acid. (*Hyposulphites.*)

Hyposulphites when fused with sodium carbonate on charcoal and a portion of the fused mass is placed on a silver coin and moistened with water produce a brownish or black stain on the coin.

Hydrochloric acid or sulphuric acid added to a hyposulphite causes the evolution of sulphurous anhydride (odor of burning sulphur) and a milkiness due to the separation of sulphur.

Argentic nitrate produces a white precipitate of argentic hyposulphite, which rapidly changes to brown and finally to black argentic sulphide. As argentic hyposulphite is soluble in an excess of a hyposulphite of an alkali, precipitation occurs only when an excess of the argentic nitrate is added.

To detect sulphuric acid and other acids in the presence of

hyposulphurous acid, the latter acid must be decomposed by gently warming with hydrochloric ácid, the liquid filtered, and the tests for sulphuric acid and acids other than hydrochloric acid made in the filtrate.

Phosphoric Acid. (*Phosphates.*)

Ammonium chloride, ammonium hydroxide, and magnesium sulphate (magnesia mixture), added in turn to a solution of a phosphate, produce a white, crystalline precipitate of ammonium magnesium phosphate.

Ammonium molybdate, added in excess with a considerable quantity of nitric acid, produces a yellow precipitate of ammonium phosphomolybdate.

(If arsenic acid is present, it must be completely removed by precipitation with hydrogen sulphide before testing for phosphoric acid. With reference to the behavior of silicic acid with ammonium molybdate, see 3, page 70.)

Boric Acid. (*Borates.*)

Turmeric paper dipped in an aqueous solution of boric acid, or of a borate acidified with hydrochloric acid, and warmed until dry, becomes reddish brown in color.

Boric acid alone, or borates placed in a dish and moistened with a few drops of concentrated sulphuric acid, covered with alcohol, and the latter ignited, impart a greenish color to the flame. (Other substances, as copper, which might also impart a green color to the flame should be removed before making the test.)

Hydrofluoric Acid. (*Fluorides.*)

Etches glass (see 4, page 67).

Carbonic Acid. (*Carbonates.*)

On adding an acid to a carbonate, effervescence occurs, due to the evolution of carbon dioxide. The presence of carbon

dioxide is confirmed by the production of a white turbidity or precipitate, due to the formation of calcium carbonate with clear calcium hydroxide solution (see 2, page 68).

Silicic Acid. (*Silicates.*)

A portion fused in a bead of microcosmic salt yields a bead in which the silica is not dissolved, but swims in the fused bead as small opaque particles (see 4, page 70).

Arsenious Acid. (*Arsenites.*)
Arsenic Acid. (*Arseniates.*)
Chromic Acid. (*Chromates.*)

These will have been detected in the preliminary examination and in the examination for bases.

Argentic nitrate added to a solution of arsenious acid, followed by the addition of ammonium hydroxide, drop by drop, or to a solution of an arsenite, produces a yellow, curdy precipitate of argentic arsenite, soluble in ammonium hydroxide and in nitric acid.

Argentic nitrate added to a solution of arsenic acid, followed by the addition of ammonium hydroxide, drop by drop, or to a solution of an arseniate, produces a reddish-brown precipitate of argentic arseniate, soluble in ammonium hydroxide and in nitric acid.

Arsenious acid may be detected in the presence of arsenic acid by its being immediately precipitated as arsenious sulphide by hydrogen sulphide, whereas arsenic acid is precipitated only after continuing the introduction of hydrogen sulphide for some time.

Arsenic acid is detected in the presence of arsenious acid by the formation of a white, crystalline precipitate of ammonium magnesium arseniate on the addition of magnesia mixture (see 7, page 28). Arsenious acid does not produce a precipitate with magnesia mixture.

Chromic acid produces a yellow precipitate with plumbic acetate and a purplish-red precipitate with argentic nitrate (see 3, page 71, and 4, page 72).

Oxalic Acid. (*Oxalates.*)

Tartaric Acid. (*Tartrates.*)

Produce white precipitates with calcium chloride. They may be distinguished when together by the behavior of their calcium salts: calcium oxalate is insoluble and calcium tartrate soluble in acetic acid.

Hydrochloric Acid. (*Chlorides.*)

Hydrobromic Acid. (*Bromides.*)

Hydriodic Acid. (*Iodides.*)

Hydrocyanic Acid. (*Cyanides.*)

All are precipitated by argentic nitrate respectively as chloride, bromide, iodide, and cyanide of silver, and are distinguished by the behavior of their silver salt with ammonium hydroxide. Argentic chloride and argentic cyanide are easily soluble in dilute ammonium hydroxide. Argentic bromide is soluble in concentrated ammonium hydroxide; argentic iodide is insoluble in ammonium hydroxide.

If the precipitate produced on the addition of argentic nitrate is insoluble in nitric acid but soluble in ammonium hydroxide, hydriodic acid is absent, but hydrochloric acid, hydrocyanic acid, and hydrobromic acid may be present. A test for hydrocyanic acid may be made by means of the Prussian-blue reaction (see 4, page 78), and for hydrobromic acid with chlorine-water and chloroform or carbon disulphide (see 5, page 75).

If neither hydrobromic acid nor hydrocyanic acid is present, the solubility of the silver precipitate in ammonium hydroxide proves the presence of hydrochloric acid. If hydrobromic acid or hydrocyanic acid is present, the distillation test with

potassium bichromate and sulphuric acid must be made for hydrochloric acid (see 4, page 74).

If the precipitate is insoluble or only partly soluble in ammonium hydroxide, the presence or absence of hydriodic acid must be established by means of chlorine-water and chloroform or carbon disulphide (see 5, page 76). If a violet color is produced, chlorine-water is added drop by drop until either decolorization occurs (absence of hydrobromic acid) or the yellow color, due to the presence of bromine (which was obscured by the violet color produced by iodine), appears (see 5, page 75).

The test for hydrocyanic acid should be made as before described (page 125). The distillation test for the detection of hydrochloric acid is to be employed when, in addition to hydriodic acid, hydrobromic acid or hydrocyanic acid is present. If hydrobromic acid or hydrocyanic acid is absent, hydrochloric acid may be detected in the presence of hydriodic acid by the solubility of the silver precipitate in ammonium hydroxide.

It should be remembered that chloride, bromide, iodide, and cyanide of silver are soluble in hyposulphites of the alkalies; therefore in the presence of hyposulphites the hyposulphurous acid should be removed by gently warming with nitric acid.

As argentic nitrate fails to produce a precipitate in solutions of mercuric cyanide, the presence of mercuric cyanide must be proved according to 4, page 111.

Hydroferrocyanic Acid. (*Ferrocyanides.*)

Ferric chloride produces a dark-blue precipitate of ferric ferrocyanide (Prussian blue), insoluble in acids (see 5, page 80).

Cupric sulphate produces a precipitate of brownish-red cupric ferrocyanide.

Hydroferricyanic Acid. (*Ferricyanides.*)

Ferrous sulphate precipitates blue ferrous ferricyanide (Turnbull's blue), insoluble in acids.

Ferric chloride fails to produce a precipitate, but produces a dark coloration in the liquid, due probably to the production of ferric ferricyanide (see 3, page 80).

Cupric sulphate precipitates greenish-yellow cupric ferricyanide.

Hydriodic acid (*iodides*), *hydrobromic acid* (*bromides*), and *hydrochloric acid* (*chlorides*) are detected in the presence of hydroferrocyanic acid and hydroferricyanic acid by means of chlorine-water and chloroform, and by distillation with potassium bichromate and sulphuric acid.

To detect hydrocyanic acid in the presence of hydroferrocyanic acid and hydroferricyanic acid, the solution is acidulated with hydrochloric acid, and calcium carbonate is immediately added until carbon dioxide ceases to be evolved. A test for hydrocyanic acid is then made by the ammonium sulphocyanide reaction (see 5, page 78). The hydrochloric acid liberates hydrocyanic acid as well as hydroferrocyanic acid and hydroferricyanic acid, but only the two latter possess the property of decomposing carbonates to form salts; hydrocyanic acid, therefore, remains in the free state.

Hydrogen Sulphide. (*Sulphides.*)

The presence of sulphides is detected when making the preliminary examination.

A soluble sulphide placed on a clean silver coin and moistened with a few drops of water produces a brownish or black stain on the coin.

Nitric acid or nitro-hydrochloric acid decomposes sulphides, with the separation of sulphur; hydrochloric acid causes the

evolution of hydrogen sulphide if it should have any action at all.

Plumbic acetate produces in solutions of sulphides a black precipitate of plumbic sulphide.

Sodium nitro-prusside solutions are colored violet by sulphides, but not by free hydrogen sulphide.

Nitrous Acid. (*Nitrites.*)

On the addition of an acid to a nitrite, brownish-red fumes of nitrogen dioxide are evolved.

On adding a few drops of sulphuric acid to a solution of a nitrite, cooling the liquid, and adding ferrous sulphate, a brown or black coloration is produced (see 5, page 82).

Potassium iodide (or cadmium iodide), starch paste, and a few drops of dilute sulphuric acid added to a solution of a nitrite produce a blue coloration (see 6, page 83).

Before testing for nitric acid in the presence of nitrous acid, the nitrous acid must be decomposed by being boiled a sufficient length of time with a solution of ammonium chloride:

$$KNO_2 + NH_4Cl = KCl + N_2 + 2H_2O.$$

Hypochlorous Acid. (*Hypochlorites.*)

Hydrochloric acid decomposes hypochlorites, with the evolution of chlorine.

Plumbic acetate produces in solutions of hypochlorites at first a white precipitate of plumbic chloride, which soon becomes yellow and finally brown, due to the formation of lead dioxide (see 3, page 83).

Nitric Acid. (*Nitrates.*)

On adding a small quantity of concentrated sulphuric acid to a solution of a nitrate, cooling, and placing a crystal of ferrous sulphate in the liquid, a brownish or black ring is formed around the crystal (see 3, page 84).

With potassium iodide (or cadmium iodide), starch paste, and dilute sulphuric acid nitrates do not produce a blue discoloration unless a fragment of metallic zinc is added. (Distinction from nitrites. See 4, page 84.)

Before testing for nitric acid in the presence of hydriodic acid or hydrobromic acid, the two latter acids must be removed by precipitation with argentic sulphate or with plumbic acetate, the precipitate filtered off, and the tests for nitric acid made in the filtrate.

Chloric Acid. (*Chlorates.*)

On warming a solution of a chlorate with hydrochloric acid the liquid becomes greenish yellow in color, and greenish-yellow fumes of a mixture of chlorine and chlorine tetroxide are evolved.

Concentrated sulphuric acid poured upon a very small portion of a solid chlorate causes the evolution of chlorine tetroxide (see 4, page 86).

Chlorates in the solid state on being strongly heated are converted into chlorides. On dissolving the residue in water and testing for a chloride with argentic nitrate, a white precipitate of argentic chloride will be produced. (A chlorate itself, free from chlorides, does not yield a precipitate with argentic nitrate.)

Acetic Acid. (*Acetates.*)

On adding ferric chloride to a solution of an acetate and boiling the liquid, a brownish-red precipitate of basic ferric acetate is formed.

Sulphuric acid added to an acetate and the liquid warmed liberates acetic acid, which is recognized by its odor of vinegar.

Alcohol added to a cooled solution of an acetate containing free sulphuric acid and then warmed produces acetic ether, which is recognized by its apple-like odor (see 6, page 87).

APPENDIX.

BEHAVIOR OF THE COMPOUNDS OF THE RARE ELEMENTS.

The deportment of the rare elements and their compounds when subjected to the usual preliminary examination, as well as the behavior of these elements with the ordinary group reagents, will be treated of in the following pages. It is not intended to give a detailed description of the separation of the rare elements from one another or from the more frequently occurring elements, but in the latter part of the appendix a few examples are given of the separation of the rare elements in minerals which may be easily procured.

I. BEHAVIOR IN THE PRELIMINARY EXAMINATION.

(*a*) On heating the substance in a glass reduction-tube:

Titanic acid becomes yellow to brown.

Niobic acid becomes yellow.

Tantalic acid becomes pale yellow.

Selenium and *selenides* yield a reddish-brown sublimate: a portion heated in a tube open at both ends and held obliquely in the flame gives a radish-like odor.

Tellurium sublimes; heated in a tube open at both ends, it burns, producing dense white clouds.

(*b*) On heating the substance with the blowpipe flame on charcoal, there are produced:

Fused metallic globules:

Gold: yellow, ductile, without incrustation.

Thallium: white, ductile, yellow incrustation.

Indium: white, ductile, white incrustation.

Incrustation, without metallic globule:

Tellurium.

Infusible metallic masses:

Tungsten,

Molybdenum,

Platinum,

Palladium, etc.

White masses

(When heated with cobaltous nitrate solution):

Titanic acid becomes yellowish green.

Niobic acid becomes dirty green.

Tantalic acid becomes flesh color.

Beryllia becomes gray.

Brownish-red masses:

Selenium compounds.

Tellurium compounds.

When placed on a silver coin and moistened with water, a brown or black stain is produced on the coin. When treated with hydrochloric acid, hydrogen selenide and hydrogen telluride are evolved.

(*c*) On fusing the substance in a bead of microcosmic salt the following colored beads result in the

	Oxidizing Flame.	*Reducing Flame.*	
Uranium:	yellow when hot, yellowish green when cold.	Green.	
Cerium:	reddish yellow when hot, lighter reddish yellow to colorless when cold.	Colorless.	
Didymium:	colorless.	Amethyst changing to violet.	In presence of iron blood-red.
Titanium:	colorless.	Violet.	
Niobium:	colorless.	Blue or violet.	
Tungsten:	colorless.	Blue.	
Molybdenum:	colorless.	Black.	
Vanadium:	colorless.	Green.	

Gold and *platinum* are not dissolved in the bead of microcosmic salt.

(*d*) Examination in the flame.

The non-luminous flame is colored by

Lithium: carmine-red.
Rubidium: violet.
Cæsium: violet.
Indium: bluish violet.
Selenium: ultramarine-blue.
Tellurium: blue bordered with green.
Thallium: intense green.
Molybdic acid: yellowish green.

Lithium, rubidium, cæsium, indium, thallium, and *gallium* are best detected by means of the spectroscope. *Erbium* and *didymium* also furnish absorption spectra.

II. BEHAVIOR WITH THE GROUP REAGENTS.

FIRST GROUP.

Hydrochloric acid precipitates:

Thallium: as white curdy $TlCl$, thallous chloride, soluble with difficulty in water.

From alkaline solutions:

Molybdic acid: as white H_2MoO_4, molybdic acid, soluble in an excess of hydrochloric acid.

Tungstic acid: as white H_2WO_4, tungstic acid, insoluble in an excess of hydrochloric acid; becomes yellow on boiling.

Tantalic acid: as white $HTaO_3$, tantalic acid, soluble in an excess of hydrochloric acid, producing opalescence in the liquid.

SECOND GROUP.

Hydrogen sulphide precipitates:

Palladium: as black PdS, palladious sulphide.
Osmium: as brownish-black OsS, osmic sulphide.
Rhodium: as brown Rh_2S_3, rhodic sulphide.
Ruthenium: as brown Ru_2S_3, ruthenic sulphide.

Insoluble in ammonium sulphide.

(The liquid at first becomes azure-blue in color.)

Gold: as black Au_2S_3, auric sulphide.
Platinum: as brownish-black PtS_2, platinic sulphide.
Iridium: as brown Ir_2S_3, iridic sulphide.
Molybdenum: as brown MoS_3, molybdic sulphide.
(A small quantity of hydrogen sulphide colors the solution blue.)
Selenium: as yellow, which on warming changes to reddish-yellow SeS_2, selenic sulphide.
Tellurium: as brown TeS_2, telluric sulphide.

Soluble in ammonium sulphide.

The solution may become blue in color if compounds of *tungsten* or *vanadium* are present.

THIRD GROUP.

Ammonium hydroxide in the presence of ammonium chloride precipitates:

Soluble in ammonium carbonate.

Uranium: as yellow $(NH_4)_2Ur_2O_7$(?), ammonium uranate.

Indium: as white $In(OH)_3$, indic hydroxide, soluble in NaOH.

Beryllium: as white $Be(OH)_2$, beryllic hydroxide, soluble in NaOH.

Zirconium: as white $Zr(OH)_4$, zirconic hydroxide, insoluble in NaOH.

Thorium: as white $Th(OH)_4$, thoric hydroxide, insoluble in NaOH.

Yttrium: as white $Y(OH)_2$, yttric hydroxide, insoluble in NaOH.

Cerium:
Lanthanum: as basic salts.
Didymium:

Titanium: as white $Ti(OH)_4$, titanic hydroxide.

Tantalum: as white $TaO_2(OH)$, acid tantalic hydroxide, or as an acid ammonium salt.

Niobium: as white $NbO_2(OH)$, acid niobic hydroxide, or as an acid ammonium salt.

FOURTH GROUP.

Ammonium sulphide precipitates:

Thallium: as black TlS, thallous sulphide.

If the filtrate from the Fourth Group precipitate is treated with hydrochloric acid, there will be precipitated:

Tungsten: as brown WS_3, tungstic sulphide.

Vanadium: as brown vanadium sulphide, containing oxygen and varying in composition.

Molybdenum: (if present) as brown MoS_3, molybdic sulphide.

FIFTH GROUP.

In this group may be found:

Lithium.

Cæsium.

Rubidium.

(To be detected by means of the spectroscope.)

III. EXAMPLES FOR PRACTICE.

WOLFRAMITE.

Wolframite may be recognized by the blue color it imparts to the bead of microcosmic salt in the reducing flame, and by the yellow residue of tungstic acid remaining when the finely-pulverized mineral is boiled with hydrochloric acid.

The finely-pulverized wolframite is boiled with concentrated hydrochloric acid, and a few drops of concentrated nitric acid are added from time to time, until the undissolved residue is pure yellow in color and does not undergo further change. Tungstic acid remains undissolved as a yellow powder, while the bases enter into solution as chlorides. The liquid containing the insoluble residue is evaporated to dryness on a water-bath, the residue extracted with water containing a small quantity of hydrochloric acid, filtered, and the filtrate tested for bases.

The insoluble residue contains tungstic acid, and frequently silicic acid and niobic acid. The residue is treated with ammonium hydroxide, which dissolves the tungstic acid as an

ammonium salt, leaving an undissolved residue consisting of silicic acid and possibly niobic acid. This residue is thoroughly washed with ammonium hydroxide, to render it free from tungstic acid, and then tested in a bead of microcosmic salt for niobic acid.

The ammoniacal solution containing ammonium tungstate should give the following reactions:

Hydrochloric acid precipitates white H_2WO_4, tungstic acid, which, on boiling, becomes yellow.

Metallic zinc and an excess of hydrochloric acid impart to the precipitate of tungstic acid a blue color changing to brown (due to the formation of lower oxides of tungsten).

Stannous chloride produces a yellow precipitate; on adding hydrochloric acid and warming, the yellow color changes to blue.

Ammonium sulphide added to the solution of ammonium tungstate produces no precipitate, but forms the soluble sulpho-salt $(NH_4)_2WS_4$. On adding hydrochloric acid to this solution, brown WS_2, tungstic sulphide, is precipitated. The supernatant liquid is generally blue in color.

MOLYBDENITE.

Molybdenite, when fused in a bead of microcosmic salt, yields a colorless bead in the oxidizing flame and a black bead in the reducing flame. It imparts a yellowish-green color to the non-luminous flame. When heated on charcoal, it yields a reddish-brown mass. It is soluble in nitro-hydrochloric acid, imparting a green color to the liquid. On evaporating the excess of acid, diluting with water, and conducting hydrogen sulphide into the solution, a blue coloration is produced, and gradually brownish-black MoS_3, molybdic sulphide, is precipitated. Molybdic sulphide is soluble in

ammonium sulphide, which dissolves it as a sulpho-salt, $(NH_4)_2MoS_4$, from which solution it is reprecipitated by hydrochloric acid as MoS_3, molybdic sulphide.

The filtrate from the precipitate produced by the introduction of hydrogen sulphide may still contain molybdenum in solution; therefore, before testing for the metals of the Fifth Group, ammonium hydroxide is added to the solution, which is gently warmed, filtered if a precipitate be formed, and the solution, which now contains $(NH_4)_2MoS_4$, is treated with hydrochloric acid, which precipitates the remaining molybdenum as molybdic sulphide.

The molybdic sulphide reprecipitated in the Second Group from the ammonium sulphide solution by hydrochloric acid is collected on a filter, dried, and placed in an uncovered crucible, which is placed obliquely over the flame and gently heated, whereby the molybdic sulphide is oxidized and converted into molybdic acid, with the evolution of sulphurous anhydride. When the sulphurous anhydride ceases to be evolved, the yellow residue is dissolved in ammonium hydroxide and the resulting solution of ammonium molybdate tested as follows: a small portion of the solution is tested for copper with a few drops of ammonium sulphide, and the remainder of the solution is used in making the tests for molybdenum. (The precipitated molybdic sulphide obtained from the Fourth Group is heated in an uncovered crucible and treated in the same manner.)

Hydrochloric acid causes the precipitation of white H_2MoO_4, molybdic acid, soluble in an excess of hydrochloric acid. Stannous chloride produces in the hydrochloric acid solution of molybdic acid a blue coloration, changing to green and finally to brown; metallic zinc produces a similar coloration, but not so promptly. The change in color in the two preceding reactions is due to the reduction of molybdic acid.

Ammonium sulphocyanide added to the ammoniacal solution, followed by the addition of hydrochloric acid and zinc, produces a carmine-red coloration (in consequence of reduction with the formation of sulphocyanides of the oxides).

Concentrated nitric acid and sodium hydrogen phosphate added to the ammoniacal solution precipitate yellow ammonium phosphomolybdate.

WULFENITE.

Wulfenite, when heated in the blowpipe flame on charcoal, yields a globule of metallic lead; when fused in a bead of microcosmic salt, it yields a colorless bead in the oxidizing flame and a black bead in the reducing flame.

Wulfenite is soluble in hydrochloric acid with the separation, upon cooling, of crystalline plumbic chloride. The hydrochloric acid solution yields with hydrogen sulphide in the Second Group a precipitate of molybdic sulphide, soluble in ammonium sulphide, thus furnishing a means of separating it from plumbic sulphide, which is insoluble in ammonium sulphide. After precipitating the Fourth Group, the reddish-brown filtrate is treated with hydrochloric acid to precipitate the remainder of molybdic sulphide.

The molybdic sulphide is further examined as given under Molybdenite, page 134.

URANINITE (PITCHBLENDE).

Uraninite, when fused in the bead of microcosmic salt, yields a yellow bead in the oxidizing flame and a green bead in the reducing flame; treated with nitric acid it dissolves, leaving a residue of silicic acid and insoluble oxides (see page 110). The nitric acid solution yields in the Third Group a precipitate containing uranium, the uranium being precipitated as yellow ammonium uranate. In order to separate

uranium the precipitate of the Third Group is digested at a moderate heat with a concentrated solution of ammonium carbonate; uranium enters into solution as uranyl ammonium carbonate, $UrO_2CO_3((NH_4)_2CO_3)_2$, imparting a yellow color to the solution.

The oxides of the other metals remain undissolved, and after being collected on a filter may be examined according to the usual scheme of analysis.

To detect uranium a portion of the yellow filtrate containing uranyl ammonium carbonate is acidulated with acetic acid and treated with potassium ferrocyanide: a reddish-brown precipitate of $(UrO_2)_2Fe(CN)_6$, uranyl ferrocyanide, indicates the presence of uranium. The remainder of the solution of uranyl ammonium carbonate is carefully concentrated on a water-bath, and on cooling glistening yellow crystals of uranyl ammonium carbonate separate, which when strongly ignited leave a residue of dark-green uranous-uranic oxide, Ur_3O_8.

On treating the filtrate containing ammonium sulphide from the precipitate of the Fourth Group with hydrochloric acid, nickelous sulphide together with vanadic sulphide may be precipitated. If a precipitate is obtained by treatment with hydrochloric acid, it is collected on a filter, washed, dried, mixed with potassium nitrate, fused, and the resulting fused mass extracted with water, whereby vanadium as an acid vanadium salt enters into solution. On filtering, neutralizing the filtrate with nitric acid, and adding a concentrated solution of ammonium chloride, vanadic acid in combination with ammonium is gradually precipitated as a white ammonium salt. On collecting the precipitate on a filter, dissolving in water, and adding a small quantity of hydrochloric acid,[1]

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[1] The solution becomes yellow or red in color.

followed by the addition of metallic zinc, the solution becomes blue in color.

RUTILE (TITANIFEROUS IRON).

Rutile, when fused in a bead of microcosmic salt in the reducing flame, yields a violet- to blood-red-colored bead. Fused in the oxidizing flame (when a sufficient quantity of the mineral is employed) it yields microscopic tabular crystals of anatase (TiO_2).

The mineral is best decomposed by being fused with acid potassium sulphate at not too high a temperature. The fused mass after cooling is pulverized and dissolved in cold water: the titanium enters into solution as sulphate. The liquid is filtered and a portion of the filtrate tested with metallic zinc or tin for titanic acid: in the presence of titanic acid a pale violet or a blue coloration is imparted to the solution and afterwards a blue precipitate separates which gradually changes to white.

On boiling the remainder of the precipitate for some time, meta-titanic acid separates as a white powder. The meta-titanic acid is filtered off and the filtrate diluted with water and again boiled and filtered. The filtrate is then tested for the remaining bases in the usual manner.

BERYL.

Beryl, when fused in a bead of microcosmic salt, slowly dissolves without the formation of a skeleton of silica. The fragment of beryl remains in the bead of microcosmic salt and gradually diminishes in size, forming, on cooling, an opalescent bead. Varieties of beryl containing chromium (for example, emeralds) impart a green color to the bead.

As beryl is insoluble in acids, it must be decomposed by fusing with sodium potassium carbonate. The fused mass is

treated with hydrochloric acid and evaporated to dryness on a water-bath, in order to separate silicic acid. The residue is extracted with water containing a small quantity of hydrochloric acid and filtered; the filtrate contains $BeCl_2$, beryllium chloride. On the addition of ammonium hydroxide to the filtrate, $Be(OH)_2$, beryllium hydroxide, separates as a white precipitate, and is collected on a filter and dissolved in an excess of sodium hydroxide. The sodium hydroxide solution contains sodium aluminate and sodium beryllate, and may also contain sodium chromite, in which case the solution would be green in color.

If chromium is not present, the solution is treated with a considerable quantity of ammonium chloride, which precipitates aluminium hydroxide and beryllium hydroxide. On boiling the liquid for some time, beryllium hydroxide enters into solution as beryllium chloride, with the evolution of ammoniacal gas, while aluminium hydroxide remains undissolved, is collected on a filter, and, when heated with cobaltous nitrate on charcoal, yields a blue mass. The filtrate, which contains beryllium chloride, is treated with ammonium hydroxide to precipitate beryllium hydroxide. Beryllium hydroxide is soluble in an excess of ammonium carbonate, and from this solution it separates on boiling as a basic beryllium carbonate. The beryllium hydroxide, when heated with cobaltous nitrate in the oxidizing flame on charcoal, yields a gray mass.

If chromium is present, the solution is diluted with water and boiled for some time: aluminium hydroxide remains in solution, while beryllium hydroxide and chromium hydroxide are precipitated. The precipitate is collected on a filter, dried, and the beryllium hydroxide separated from the chromium hydroxide by fusing with a mixture of sodium carbonate and potassium nitrate. On extracting the yellow fused

mass with water, beryllium oxide remains undissolved, while chromium enters into solution as a chromate of the alkali.

CERITE.

Cerite, heated in the blowpipe flame on charcoal, is infusible, but becomes dirty yellow in color. Fused in a bead of microcosmic salt, it yields in the oxidizing flame a reddish-yellow bead, and in the reducing flame a colorless bead, together with a skeleton of silica. On heating a portion of the finely-pulverized mineral with hydrochloric acid, diluting with water, filtering, and adding oxalic acid to the filtrate, a white precipitate is produced.

On heating the mineral with concentrated hydrochloric acid, evaporating to dryness on a water-bath, and extracting the residue with water and a few drops of hydrochloric acid, the bases enter into solution while silicic acid remains undissolved.

In the Second Group, in addition to other metals, molybdenum may be precipitated as molybdic sulphide. (See Molybdenite, page 134.)

Cerium, lanthanum, and didymium are precipitated by ammonium hydroxide in the Third Group as hydroxides: $Ce(OH)_2$, $La(OH)_2$, and $Di(OH)_2$. Cerium hydroxide and lanthanum hydroxide are white. The former when exposed to the air oxidizes and becomes yellow; didymium hydroxide is pink in color. On collecting the precipitate of the Third Group on a filter, dissolving in hydrochloric acid, and adding oxalic acid, cerium, lanthanum, and didymium are precipitated as white oxalates insoluble in dilute acids; the filtrate from the precipitate of oxalates may be examined for the remaining bases of the Third Group.

The oxalates of cerium, lanthanum, and didymium when ignited yield a brown residue consisting of a mixture of

oxides (Ce_3O_4, LaO, and DiO). On heating a portion of this mixture of oxides with concentrated sulphuric acid, sulphates are formed which are soluble in water and impart a yellow color to the liquid. In this solution concentrated potassium sulphate produces a lemon-yellow precipitate consisting of a mixture of double salts.

The remainder of the mixture of oxides is treated with hydrochloric acid and alcohol and then heated: the oxides are dissolved thereby, with the formation of chlorides ($CeCl_2$, $LaCl_2$, $DiCl_2$). If didymium is present, on passing a ray of light through the solution, the spectrum shows dark absorption bands (four between Frauenhofer's lines D and F and two between F and G).

On adding sodium acetate and passing chlorine through the solution, or on the addition of sodium hypochlorite, light-yellow $Ce_3O_7H_6$, cerium hydroxide, is precipitated, which is soluble when warmed with hydrochloric acid, forming $CeCl_2$, with the evolution of chlorine. (For the separation of cerium, lanthanum, and didymium the reader is referred to more extensive works on qualitative analysis.)

ZIRCON (HYACINTH).

Zircon, heated in the blowpipe flame on charcoal, is infusible, but becomes lighter in color. It is not dissolved in the bead of microcosmic salt.

It is decomposed by being fused for some time with sodium potassium carbonate. The fused mass is treated with hydrochloric acid, evaporated to dryness on a water-bath (to render the silica insoluble), the residue extracted with water and hydrochloric acid and filtered. The filtrate contains zirconium as zirconium chloride. From this solution the zirconium is precipitated by ammonium hydroxide in the Third Group as $Zr(OH)_4$, zirconium hydroxide. Zirconium hy-

droxide is insoluble in sodium hydroxide, but soluble in ammonium carbonate. From the solution in ammonium carbonate it is reprecipitated by boiling.

On dissolving a portion of this precipitate in sulphuric acid and adding a concentrated solution of potassium sulphate, a white double salt of zirconium is precipitated.

The hydrochloric acid solution is not precipitated by oxalic acid, but the neutral solution is precipitated by ammonium oxalate; the precipitate redissolves in an excess of ammonium oxalate. Turmeric paper, moistened with the hydrochloric acid solution, becomes reddish brown in color when dry.

LEPIDOLITE.

Lepidolite when fused in a bead of microcosmic salt yields a skeleton of silica. When placed on a platinum wire and held in the non-luminous flame it imparts a carmine-red color to the flame, especially after moistening the lepidolite with a few drops of hydrochloric acid. Treated with concentrated sulphuric acid it responds to the fluorine reactions (see 4, page 67, and 5, page 68).

A portion of the mineral is heated in a platinum crucible (without the addition of carbonates of the alkalies as a flux) until melted. The fused mass is pulverized and then decomposed by being boiled with concentrated hydrochloric acid. The solution is evaporated to dryness on a water-bath to render the silica insoluble; the residue is extracted with water and a few drops of hydrochloric acid, the insoluble silica filtered off, and the filtrate examined for bases.

Lithium belongs to the Sixth Group. The hydrochloric acid filtrate, obtained as described above, is treated with ammonium carbonate to precipitate the metals of the Fifth Group, and with sodium hydrogen phosphate to precipitate magnesium, filtered, the filtrate treated with barium chloride,

and the liquid again filtered. The filtrate now contains, in addition to the excess of barium chloride, the alkaline metals as chlorides. The liquid is evaporated to dryness, the residue gently heated over a free flame to expel ammonium chloride, and then placed in a small flask and extracted with a mixture of alcohol and ether. Lithium chloride enters into solution, while the chlorides of the other metals remain undissolved.

The alcoholic solution is filtered and the filtrate evaporated to dryness on a water-bath; the residue remaining consists of lithium chloride, which is recognized by its imparting a carmine-red color to the non-luminous flame and by the examination with the spectroscope. The residue, insoluble in the mixture of alcohol and ether, is dissolved in water, and sulphuric acid added to the solution to precipitate barium as barium sulphate, which is filtered off and the filtrate examined for potassium and sodium.

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